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REFERENCE

Lane, B. H., 1935. Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C., 25c.)

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American Journal of Science

MARCH 1952

A PORTION OF THE SYSTEM CALCIUM CARBONATE-CARBON DIOXIDE-WATER, WITH GEOLOGICAL IMPLICATIONS *

JOHN P. MILLER

ABSTRACT. The solubility of $CaCO_3$ in water depends on the presence of CO_2, the concentration of which is a function of temperature and pressure of CO_2 in equilibrium with the water. As CO_2-pressure increases at constant temperature the solubility of $CaCO_3$ increases, and at constant CO_2-pressure the solubility of $CaCO_3$ increases with decreasing temperature. In the present investigation 259 determinations of solubility were made at temperatures ranging from 0° to 105° C. and at CO_2-pressures ranging from 1 to 100 bars. Three types of $CaCO_3$,—optical grade calcite, Solenhofen limestone, and *Venus mercenaria* shells—were used for the experiments. Solvents were distilled water, 0.5 M. NaCl solution, and standard sea water. Solubility was determined by loss in weight of plates of $CaCO_3$. Solenhofen limestone is more soluble than optical calcite, and the shells are more soluble than Solenhofen limestone. The effect of NaCl solution or sea water is to increase the solubility of all kinds of $CaCO_3$ tested. The data obtained in the present investigation compare favorably with the results of earlier investigations, though in general the solubility values of the present study are somewhat higher. These discrepancies are attributed to differences in techniques and materials used for determination of solubility. These data are not readily adaptable to problems of solubility under surface conditions because the experimental CO_2-pressures are much greater than the partial pressure of CO_2 in equilibrium with surface and ground water. Calculation of equilibrium constants for the reaction through the range of CO_2-pressures studied experimentally makes possible extrapolation of the data for solubility of $CaCO_3$ to conditions of low CO_2-pressures insofar as data for solubility of CO_2 are available. As for so many simple laboratory experiments, direct application of the data obtained to natural processes is complicated by numerous factors of unknown magnitude. It is concluded that the data presented here, though as precise as careful technique can make them, include too few components of natural systems to permit drawing any far-reaching conclusions regarding the nature and rates of geologic processes.

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INTRODUCTION

SEVERAL geological problems involve the solubility of calcium carbonate in carbon dioxide and water. If laboratory research is to contribute data to solve these problems, it is obvious that such data should be precise. Only by use of pure reagents and carefully controlled experimental conditions can precision be attained. However, such restrictions are not imposed in Nature. Calcium carbonate occurs in many more or less impure forms, and moreover, aqueous solutions containing carbon dioxide usually contain other substances both organic and inorganic. Temperature and pressure conditions at or near the earth's surface range widely. Laboratory experiments can, therefore, furnish only a model of the manner in which the reactions in nature may take place. Nevertheless, experimental data may provide valuable guides to a more complete understanding of geological processes.

The experiments here recorded cover a portion of the system $CaCO_3$ – CO_2 – H_2O for temperatures ranging from 0 to 105°C. and CO_2-pressures from 1 to 100 bars.[1] Some additional data are given for the solubility of $CaCO_3$ in NaCl solution and in sea water.

Chemical Nature of the Solubility of Calcium Carbonate

For more than two centuries it has been known that the solubility of calcium carbonate in water is dependent on the presence of carbon dioxide. It is now generally believed that carbon dioxide combines with water to form carbonic acid which in turn reacts with calcium carbonate to form the soluble bicarbonate,[2] according to the following equilibria:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + (HCO_3)^-$$

$$CaCO_3 + H^+ + (HCO_3)^- \rightleftharpoons \underset{\text{in solution}}{Ca^{++} + 2(HCO_3)^-}$$

The theory for these equilibria, including the derivation of certain useful constants, such as ionization constants and the solubility product, has been developed by Walker and Cornack (1900), Bodländer (1900), Steiglitz (1909), Tillmans and Heublein (1912), and Johnston (1915).

The solubility of calcium carbonate as a function of CO_2-

[1] One bar equals 0.9869 normal atmosphere.

[2] Though $Ca(HCO_3)_2$ cannot be isolated in the solid form at room temperature, it is, nevertheless, considered to exist in solution as Ca^{++} and HCO_3^- ions. See Kelser and Leavitt (1908).

concentration depends upon (1) temperature, and (2) pressure of CO_2 in equilibrium with the water. As CO_2-pressure increases at constant temperature solubility of $CaCO_3$ increases. On the other hand, at constant CO_2-pressure the solubility of $CaCO_3$ increases with decreasing temperature. In water free of CO_2, solubility of $CaCO_3$ is exceedingly small. Kennedy[3] has recently observed that at a temperature of approximately 300°C. calcite is even less soluble in pure water than is quartz.

Carbon dioxide concentrations in nature range widely. The atmosphere contains 3.0 to 3.5 parts CO_2/10,000 or a partial pressure of $3.0 - 3.5 \times 10^{-4}$ atmospheres. Because of this atmospheric CO_2-pressure many surface waters have some capacity as solvents for $CaCO_3$. There are, however, several processes which tend to enrich or deplete the amount of CO_2 in natural waters. Falling rain entrains and absorbs CO_2 in excess of its normal atmospheric quota. Surface water standing in the presence of decaying organic matter becomes enriched in CO_2. Ground water in the vadose zone may have a high CO_2-content because soil bacteria provide CO_2. On the other hand, photosynthesis, agitation of the water, or an increase in temperature will result in loss of CO_2. In general the concentrations of CO_2 present in natural surface waters are so small as to be extremely difficult to duplicate in laboratory experiments. The CO_2-pressure range of 1 – 100 bars covered in the current research was chosen in order to avoid such experimental difficulties. Though the data obtained thereby are not directly applicable to problems involving the solubility of $CaCO_3$ in surface waters, they do at least provide a sound basis for extrapolation and calculation.

Previous Investigations

During the last century, a voluminous literature bearing on the solubility of $CaCO_3$ has accumulated. For the most part, interest in the subject has stemmed from practical problems, such as methods to soften "hard" water, means to prevent boiler scale, and procedures for improving resistance of concrete to weathering. In general, the investigators who have studied the solubility of $CaCO_3$ in H_2O and CO_2

[3] Kennedy, G. C. Personal communication.

have covered relatively small ranges of temperature and CO_2-pressure, as is shown by table 1. Numerous other published data on the solubility of $CaCO_3$ in H_2O and CO_2 are omitted from table 1 for reasons given in brief annotations to the complete references. These include the work of Caro (1874), Kohlrausch and Rose (1893), Anderson (1889), Treadwell and Reuter (1896), Leather and Sen (1909), Seyler and Lloyd (1909), Cavazzi (1917), and Leick (1932).

The presence of dissolved inorganic ions affects the solubility of $CaCO_3$. Investigators who have studied the effects of other dissolved ions on the solubility of $CaCO_3$ are listed in table 2, which shows the ranges of temperature, CO_2-pressure, and salt concentrations covered. For reasons given

TABLE 1

Ranges of temperature and CO_2-pressure covered by investigations on solubility of $CaCO_3$ in H_2O and CO_2.

Investigator and Date	Range Covered	
	Temperature (°C.)	CO_2-pressure
Cossa (1869)	7.5-28.0	737-754 mm.
Schloesing (1872)	16	$5x10^{-4}$ - 0.98 atm.
Engel (1888)	15	1-6 atm.
McCoy and Smith (1911)	25	0.06-25.4 atm.
Kendall (1912)	25,50,100	$3.69x10^{-4}$ atm. ± 5 %
Wells (1915)	0-50	$3.02\text{-}3.27 \times 10^{-4}$ atm.
Johnston and Williamson (1916) (calculated)	16	$3.16x10^{-14}$ - $5.0x10^{-4}$ atm.
Cavazzi (1916)	0-15	1.0 atm.
Bäckström (1921)	9-35	744-777 mm.
Mitchell (1923)	25	4-24 atm.
Kugelmass and Shohl (1924)	38	0.0263-0.1005 atm.
Haehnel (1924)	18	1-56 atm.
	18-55	56 atm.
Stumper (1925) (calculated)	25	0.01-2.0 atm.
Kline (see Frear and Johnston — 1929)	25	0.00031-0.9684 atm.
Frear and Johnston (1929)	25	0.00032-10.0 atm.

TABLE 2

Ranges of temperature, CO_2-pressure, and salt concentration covered by investigations of $CaCO_3$ solubility as a function of temperature, CO_2-pressure, and concentration of other ions.

Investigator and Date	Range Covered		
	Temperature (°C.)	CO_2-pressure	Salt Concentration
LeBlanc and Novotny (1906)	18-100	"CO_2-free"	0.0001-0.01 N. NaOH
Cameron and Robinson (1907)	25	1.0 atm.	0.26% KCl
Cameron, Bell, and Robinson (1907)	25	1.0 atm.	1.45-35.85 g. NaCl/100 g. H_2O
Ehlert and Hempel (1912)	5	2.0 atm.	0.2300 g. $MgCl_2.6H_2O$/li.
	5-8	2.0 atm.	28.0-351.2 g. NaCl/li.
	14	2.0 atm.	105.3-sat. g. $MgSO_4.7H_2O$/li.
	14	2.0 atm.	137.7-sat. g. $Na_2SO_4.10H_2O$/li.
Mitchell (1923)	25	6-16 atm.	0.89-14.60 M. $MgCO_3.3H_2O$
Frear and Johnston (1929)	25	0.12-0.96 atm.	0.0041-0.0144 M. $CaSO_4$
	25	0.953-0.968 atm.	0.0038-0.236 M. NaCl
Halla (1935)	25-30	1.0 atm.	Ca++ = 0.17-8.67 g. moles/li. Mg++ = 2.20-221.8 g. moles/li.
Yanat'eva (1949)	25	1.0 atm.	0-2% Dolomite, gypsum, magnesite, NaCl

in annotations to the complete references, the results of the following workers are not included: Treadwell and Reuter (1898), Cameron and Seidell (1902), Cantoni and Goguelia (1905), LeBlanc and Novotny (1906), Seyler and Lloyd (1909), Rindell (1910), Warynski and Kouropatwinska (1916), Askew (1923), Pratolango (1925), Hastings, Murray, and Sendroy, Jr. (1927), Dubrisay and Francois (1931), Leick (1932), and Browman and Hastings (1937).

In addition to the investigations mentioned above, the solubility of various forms of $CaCO_3$ in sea water has been reported on by Reid (1888), Irving and Young (1888), Anderson (1889), Johnston and Williamson (1916b), Wells (1918), McClendon (1918), Irving (1926), Bavendamm (1932), Black (1933), Revelle (1934), Wattenberg (1936, 1937), Chigirin (1938), Repa and Legkova (1938), and Smith (1940).

Results of these earlier investigations that are pertinent to the data obtained by the current research are discussed in another section of this paper.

The new data presented in this paper are the result of a systematic investigation of $CaCO_3$ solubility as a function of temperature, CO_2-pressure, and concentration of other ions. As the scope of the present investigation is more inclusive than those made earlier, it should provide some basis for judging the relative merit of previous work.

PRESENT EXPERIMENTAL WORK

During the course of the present experimental work, 259 determinations of solubility of $CaCO_3$ were made. Three different types of $CaCO_3$—optical grade calcite, Solenhofen limestone, and *Venus mercenaria* shells—were used for the experiments. Distilled water, 0.5 M. NaCl solution, and standard sea water were used as solvents.

Materials.—Optical grade calcite of high purity from a locality near Manuel Benevides, Chihuahua, Mexico, was provided by Mr. Dan E. Mayers, formerly a graduate student at Harvard University. Spectrographic analysis of the calcite by Dr. Robert Allen, formerly of Harvard University, gave the results in table 3.

TABLE 3

Impurities in calcite as determined by spectrographic analysis.

Al	— 0.001-0.01%	Fe	— none detected
Ti	— 0.001-0.01%	K	— none detected
Mg	— 0.001-0.01%	Li	— none detected
V	— 0.001-0.01%	Mn	— none detected
Ba	— 0.001-0.01%	Mo	— none detected
Sr	— 0.01-0.1%	Na	— none detected
As	— none detected	Ni	— none detected
Ag	— none detected	Pb	— none detected
B	— none detected	Sb	— none detected
Bi	— none detected	Sn	— none detected
Co	— none detected	W	— none detected
Cr	— none detected	Zn	— none detected
Cu	— none detected	Zr	— none detected

Solenhofen limestone used in these experiments was analyzed spectrographically, with the results shown in table 4.

TABLE 4

Impurities in Solenhofen limestone as determined by spectrographic analysis.

Ag	— 0.001-0.01%	B	— none detected
Sn	— 0.001-0.01%	Bi	— none detected
Pb	— 0.001-0.01%	Co	— none detected
Si	— 0.01-0.1%	Cu	— none detected
Mn	— 0.01-0.1%	K	— none detected
Fe	— 0.01-0.1%	Li	— none detected
Ba	— 0.01-0.1%	Mo	— none detected
V	— 0.01-0.1%	Na	— none detected
Al	— 0.01-0.1%	Ni	— none detected
Ti	— 0.01-0.1%	Sb	— none detected
Mg	— 0.1-1.0%	W	— none detected
Sr	— 0.1-1.0%	Zn	— none detected
As	— none detected	Zr	— none detected

Venus mercenaria shells from the beach at Woods Hole, Massachusetts, were provided by Dr. Rushdi Said, formerly of Harvard University. No chemical analysis was available.

Attempts to use Rutland marble for determination of solubility were unsuccessful, as the sugary texture of this material resulted in its crumbling easily when used in small plates.

Samples of the various $CaCO_3$ materials were ground to plates approximately 1 mm. thick, 20-40 mm. long, and 10-15 mm. wide to give a large surface area per unit weight. The plates ranged in weight from 0.5 to 1.0 gram. After grinding to size and before use in determination of solubility, the

plates were washed with dilute HCl and rinsed with distilled water.

Water for these experiments was distilled in a Pyrex glass still and stored in Pyrex bottles. Standard sea water from the deep Atlantic was furnished by Dr. A. C. Redfield, Woods Hole Oceanographic Institution. From the known salinity of 36.45 parts per 1000, approximate concentrations of the ions present were calculated[4] and are given in table 5.

TABLE 5

The major constituents of sea water.

Ion	*Parts/million*
Cl^-	20,000
SO_4^-	2,790
HCO_3^-	147
Br^-	68
F^-	1
H_3BO_3	27
Na^+	11,250
Mg^{++}	1,340
Ca^{++}	422
K^+	402
Sr^{++}	14

Carbon dioxide was purchased from The Liquid Carbonic Corporation, Cambridge, Massachusetts, and was 99.85% pure CO_2; the only impurity was water. The same cylinder of CO_2 was used throughout the experiments.

Apparatus.—A diagrammatic sketch of the apparatus for measurement of solubility is shown in figure 1. It consisted of a steel bomb fitted with removable glass liner partially filled with water in which a plate of $CaCO_3$ was placed. The bomb was placed upright in a furnace, the temperature of which was carefully regulated. Capillary tubing connected the bomb to a CO_2 source at some measured pressure.

Four steel bombs, designed by Prof. G. C. Kennedy and constructed by Mr. Harold Ames, were used for these experiments. All the bombs were made of Allegheny metal, two of 12% chrome steel and the others of 25% Cr - 20% Ni steel. Corrosive properties of the latter metal were far superior.

[4] Using salinity of 36.45 parts/1000, according to the relationship,

$$\text{Salinity} = 0.03 + 1.805 \times \text{chlorinity}$$

and from tables, p. 173, Sverdrup, Johnston, and Fleming (1942).

Capacity of the four bombs ranged from 10-90 cc. During most runs, all four bombs were operated simultaneously at the same CO_2-pressure, but at different temperatures. Inside the bombs, removable glass liners, made of Pyrex test tubes, contained the $CaCO_3$ plates and water, as shown in the detail, figure 1. Glass liners were necessary in order to prevent carbonic acid from attacking and etching the steel bombs. Connections between bombs, gauge, CO_2-cylinder, etc., were made by means of stainless steel tubing 0.018 inches in diameter, fitted with cone-in-cone-type connectors. Needle valves were used to regulate the CO_2-pressure.

Nichrome-wound muffle furnaces 3 inches in diameter and 18 inches long gave a temperature difference in the bombs of less than 1° C. For most runs above 30°, the temperature was regulated by an alternating current bridge and thyratron circuit, of the type described by Bancroft (1942). Temperature was measured by the e. m. f. of an alumel-chromel thermocouple on a Leeds and Northrup Type K potentiometer. For some runs at 37°-42°, a water bath heated by a hot-plate and immersion heater regulated by a mercury switch-thyratron arrangement was used. Temperature of 0° was maintained by submerging the bombs in an ice bath, and temperatures between 0° and 30° were maintained by use of a water bath contained in an insulated jar. In all cases,

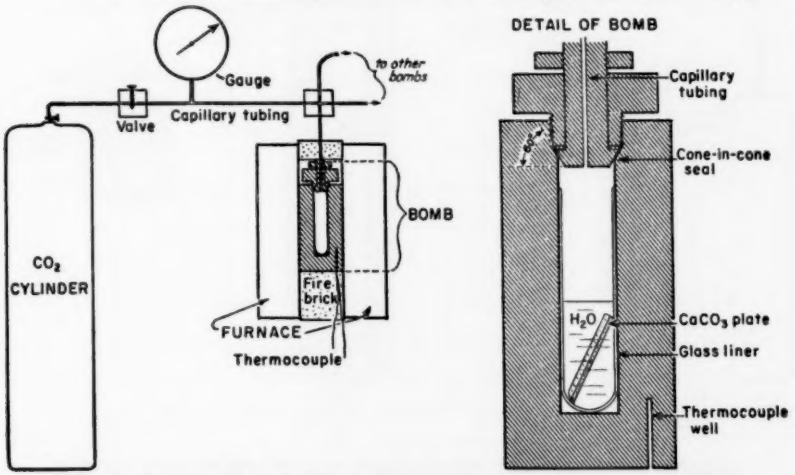

Fig. 1. Diagrammatic sketch of apparatus for determination of solubility.

temperature regulation and measurement were accurate to within 1° C.

CO_2-pressure was measured on a Heise 100-bar 15-inch Bourdon tube gauge, manufactured by the Heise Bourdon Tube Corporation, Newtown, Connecticut. The gauge was calibrated by the manufacturer against a dead weight piston gauge and had a maximum hysteresis of less than 0.1 bar. CO_2-pressures greater than cylinder pressure (64 bars at 25° C.) were achieved by use of an auxiliary compressor shown in figure 2. The compression apparatus was designed by Prof. G. C. Kennedy and Prof. Francis Birch, and constructed by Mr. Harold Ames. Operation was as follows: With all valves open, the floating piston was forced to the bottom of the compression cylinder, by tank pressure of CO_2, and the system was allowed to come to equilibrium with the CO_2-cylinder. Then with valve V_1b closed, the pump was operated. This forced kerosene into the compression cylinder, advanced the floating piston and compressed the CO_2-gas. Increase in pressure is slow until the critical pressure of 74

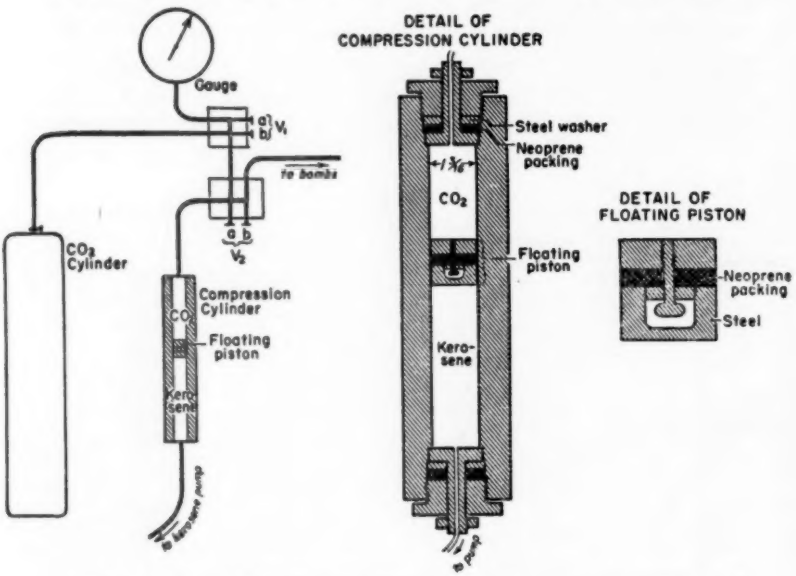

Fig. 2. Diagrammatic sketch of apparatus for determination of solubility at CO_2-pressures greater than 50 bars.

bars is reached, after which pressure increases rapidly, due to the small compressibility of liquid CO_2. As the volume of the compression cylinder was small compared with the total volume of the bombs, more than one stroke was usually required to reach the desired pressure.

The bombs, the temperature regulating and measuring equipment, and the gauges used in these experiments have been described in greater detail by Kennedy (1950a, 1950b).

Experimental procedure.—The apparatus and procedure used in the experiments were changed several times during the early stages of the investigation, and the results reported

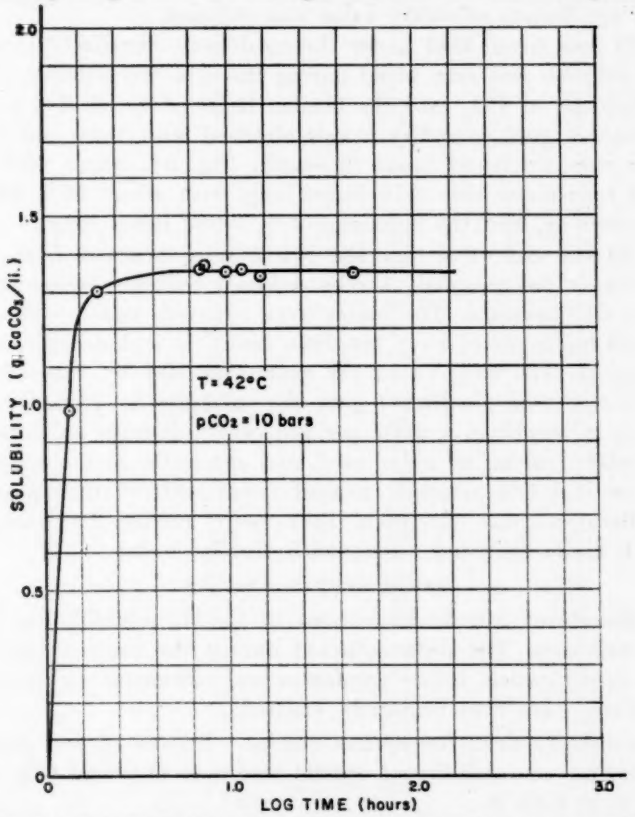

Fig. 3. Plot illustrating time required for equilibrium to be attained in the system $CaCO_3$-CO_2-H_2O.

do not include those obtained by various earlier methods, but apply only to the apparatus as sketched in figure 1 and procedure as described here.

$CaCO_3$ plates (weighed to the nearest 0.0001 g.) were placed in the glass liners and sufficient water (measured at 25° to the nearest 0.01 ml.) was added from a burette to cover the plates. The glass liners were then put into the bombs, and the bombs sealed and connected with tubes leading to the CO_2-cylinder gauge, etc. The bombs were placed in furnaces and allowed to come to constant temperature, which usually required 6-8 hours. Then CO_2 at the desired pressure was admitted into the bombs, and the run continued until an equilibrium solubility value was attained.

It was found that under the conditions described the rate of solution was very rapid during the first few minutes after admission of CO_2 into the bombs. Runs of about 6-8 hours duration gave solubility values identical with those obtained for runs up to 50 hours in length. (fig. 3). About 85% of the runs made were 8-12 hours long, with about 10% 12-36 hours long, and the remaining 5%, 36-50 hours long.

At the end of a run, the bombs were removed from the furnaces and unsealed, thereby suddenly reducing temperature and CO_2-pressure. The plates were removed, rinsed with distilled water, dried on a hotplate, cooled in a desiccator, and weighed. The weight lost (in grams) divided by the volume of water used (in liters) gave the solubility in grams/liter.[5] Loss in weight of a plate per run, which depends on the size of plate, volume of water used, and especially on the temperature and CO_2-pressure, ranged from 0.0010-0.0250 grams.

Between runs, the glass liners were cleaned by washing with dilute HCl and rinsing with distilled water.

EXPERIMENTAL RESULTS

Results of 259 determinations of $CaCO_3$ solubility are reported here. The data collected during the early stages of the investigation, before apparatus and techniques were standardized, have been purposely omitted.

Solubility data for optical calcite.—Results of 165 determinations of solubility of optical calcite in H_2O and CO_2 are given in table 6.

[5] This method of determining solubility has been described by Kennedy (1944).

TABLE 6

Solubility of optical calcite in H_2O and CO_2.

Temperature (°C.)	Solubility (g. $CaCO_3$/l.)	Temperature (°C.)	Solubility (g. $CaCO_3$/l.)
	P_{CO_2} = 1 bar		
0	1.30	54	0.40
0	1.30	61	.33
0	1.34	61	.37
23	0.85	61	.36
24	.87	70	.30
24	.86	71	.28
38	.59	84	.24
38	.59	93	.21
41	.57	99	.23
42	.50	99	.21
42	.50	101	.19
43	.48	101	.20
54	.39	104	.17
	P_{CO_2} = 10 bars		
0	2.46	61	0.97
0	2.45	67	.84
0	2.43	67	.88
23	1.81	70	.78
23	1.82	70	.83
23	1.76	71	0.77
23	1.78	77	.72
24	1.77	78	.72
25	1.75	78	.72
42	1.35	84	.66
42	1.34	84	.62
42	1.33	86	.61
42	1.37	88	.59
42	1.36	94	.57
42	1.36	94	.52
42	1.35	96	.54
50	1.14	97	.53
50	1.16	98	.55
59	1.00	99	.51
59	0.96	102	.52
59	.98	102	.52
59	.98	102	.50
60	.99	104	.50
		104	.49
	P_{CO_2} = 20 bars		
23	2.25	70	0.98
24	2.17	71	.95

TABLE 6 (continued)

Temperature (°C.)	Solubility (g. $CaCO_3$/l.)	Temperature (°C.)	Solubility (g. $CaCO_3$/l.)
	P_{CO_2} = 20 bars (continued)		
25	2.18	72	.91
42	1.64	75	.88
42	1.65	75	.86
42	1.66	88	.75
42	1.65	88	.72
42	1.66	90	.67
43	1.68	93	.66
53	1.33	94	.69
60	1.22	95	.67
60	1.20	98	.63
60	1.23	103	.57
61	1.20	104	.58
67	1.06	105	.59
		105	.56
	P_{CO_2} = 40 bars		
23	2.65	73	1.12
23	2.72	78	1.06
25	2.68	78	1.04
39	2.11	78	1.04
42	2.03	78	1.05
42	2.02	86	0.88
42	2.01	94	.80
42	2.02	99	.71
42	2.00	99	.72
54	1.54	102	.69
54	1.55	102	.70
61	1.44	105	.67
61	1.42	105	.65
61	1.45		
	P_{CO_2} = 50 bars		
25	2.90	60	1.56
42	2.16	61	1.54
42	2.15	61	1.53
42	2.20	61	1.54
44	2.09	67	1.35
50	1.82	78	1.12
50	1.86	86	0.95
51	1.79	102	.75
		104	.73

TABLE 6 (continued)

Temperature (°C.)	Solubility (g. $CaCO_3$/l.)	Temperature (°C.)	Solubility (g. $CaCO_3$/l.)
	P_{CO_2} = 100 bars		
41	2.46	78	1.26
42	2.40	78	1.27
42	2.40	78	1.29
42	2.43	87	1.06
61	1.76	87	1.09
61	1.81	100	0.88
68	1.56	102	.84
68	1.53	104	.86
		104	.82

Determinations at 0° could not be made at CO_2-pressures greater than 10 bars due to formation of the solid phase, carbon dioxide hydrate ($CO_2.8H_2O$). For the same reason, at 25°, no determinations could be made at CO_2-pressures greater than 50 bars. Villard (1894, 1897) and Wroblewski

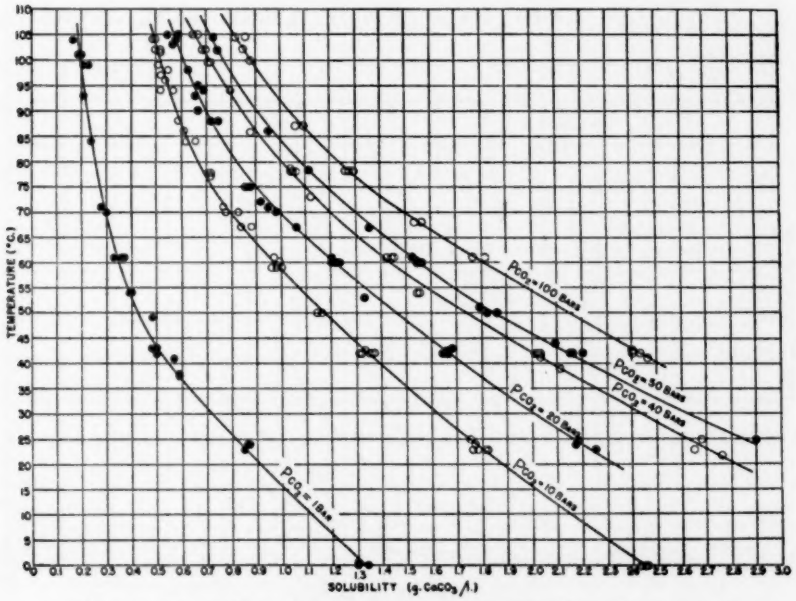

Fig. 4. CO_2-isobars in the system. $CaCO_3$-CO_2-H_2O. Data are for optical calcite.

(1892) give the following data for the decomposition pressure of the hydrate:

Temp. °C.	-6	0	0.48	2.7	3.6	5.3	6.1	6.3	6.9	10.0
P in atm. Wroblewski ..		12.3		16.7	17.9	21.8		23.3	26.1	
P in atm. Villard	6.5	12.2	12.7	16.7	17.9	21.8	23.8		26.1	44.3

The data given in table 6 were plotted with solubility ($g.CaCO_3/l.$) as the abscissa and temperature as the ordinate. Smooth curves of CO_2 isobars were drawn through the points, and the result is shown in figure 4. It will be noted that the isobaric curves in figure 4 have a negative slope, i. e., as temperature increases at constant CO_2-pressure, solubility of $CaCO_3$ decreases.

In figure 5, solubility is plotted as the abscissa and CO_2-pressure as the ordinate, and curves of isotherms are drawn at 10° intervals.

The curves of Wiebe and Gaddy (1939, 1940) for solubility of CO_2 in water are given in figure 6. By taking a series

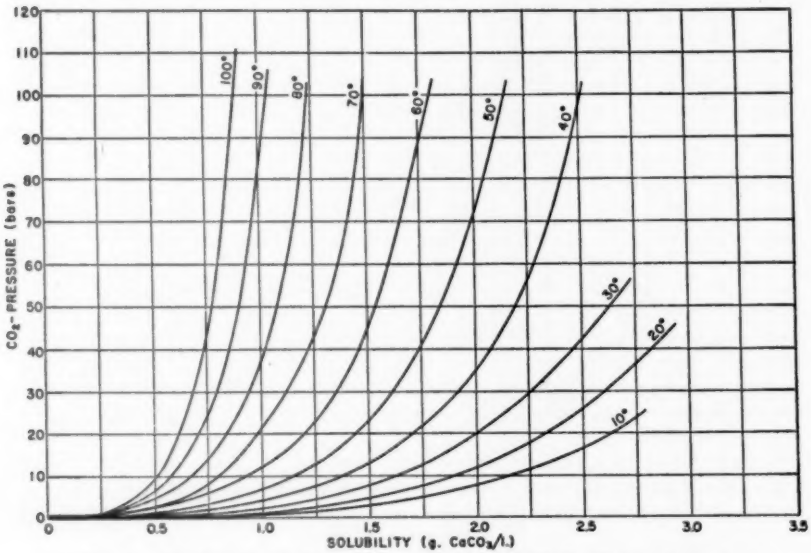

Fig. 5. Isotherms in the system $CaCO_3$-CO_2-H_2O. Data shown are for optical calcite.

of temperature and CO_2-pressure values for a constant CO_2-concentration from these curves and finding the $CaCO_3$ solubility (using figure 5) corresponding to these temperatures and CO_2-pressures, iso-concentration curves for CO_2 were plotted, with the result shown in figure 7. For example, as

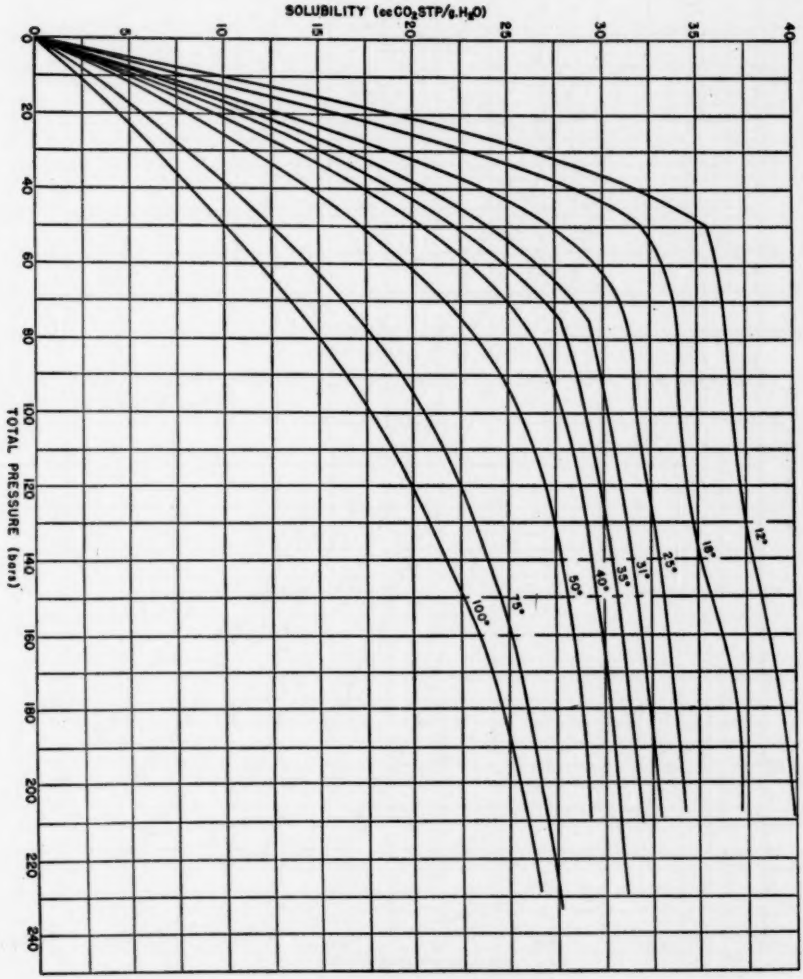

Fig. 6. Plot of Wiebe and Gaddy's (1939, 1940) data for solubility of CO_2 in H_2O.

shown in figure 6, at 50° a CO_2-pressure of 26 bars is required to maintain a solubility of 10 cc. CO_2/g. H_2O. As shown in figure 5, at this temperature and CO_2-pressure, $CaCO_3$ is soluble to the extent of 1.55 g./li. In figure 4, the negative slope of the solubility curve is evidently partially due to the

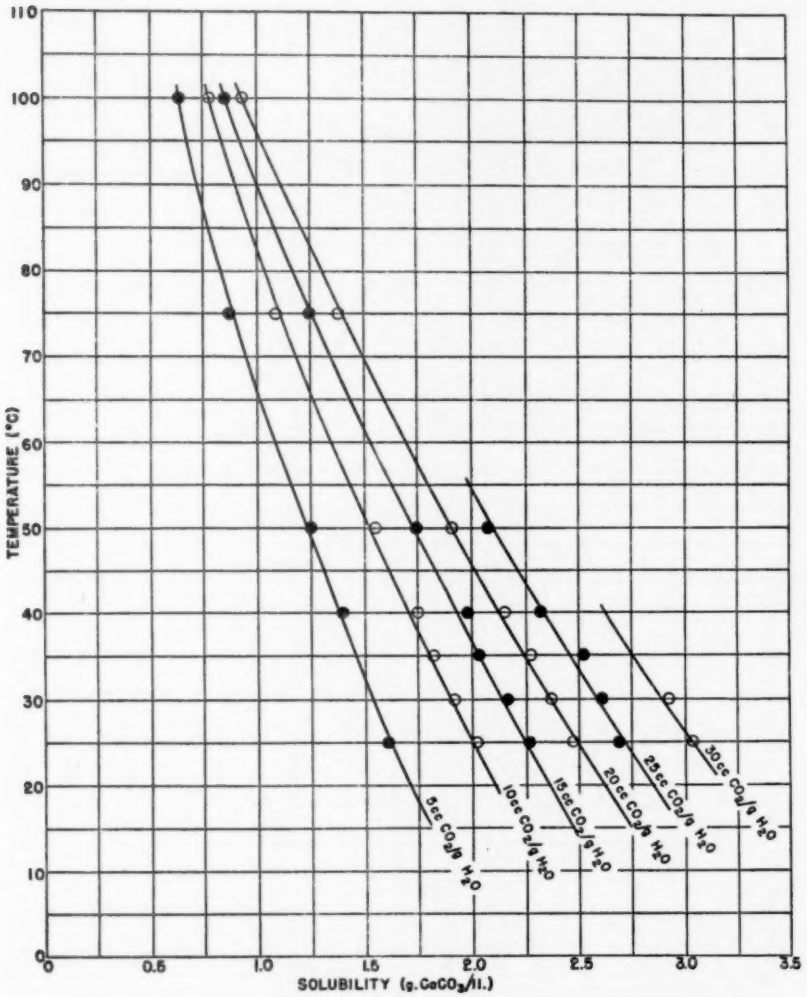

Fig. 7. CO_2 iso-concentration curves in the system $CaCO_3$-CO_2-H_2O. The data are for optical calcite.

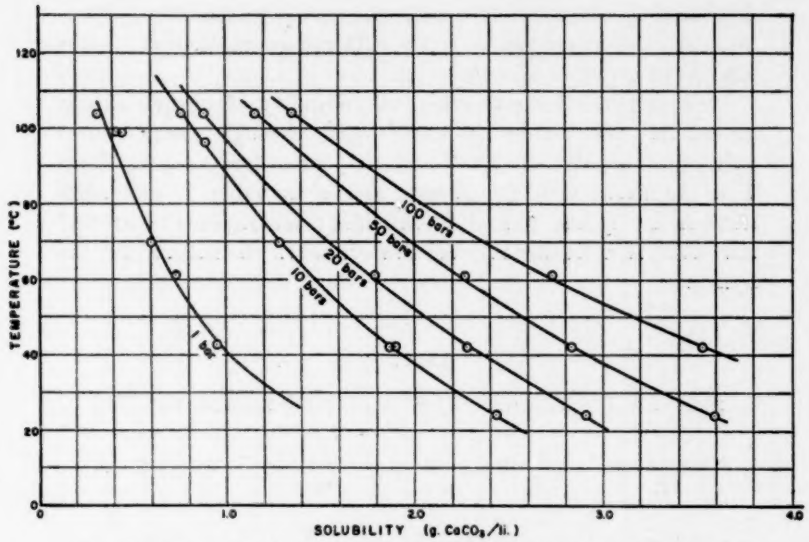

Fig. 8. Isobars in the system $CaCO_3$-CO_2-0.5 M. NaCl. The data are for optical calcite.

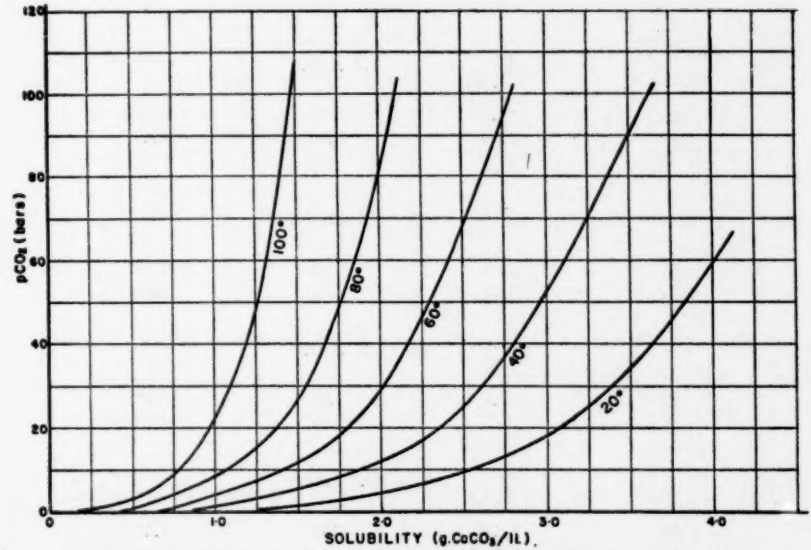

Fig. 9. Isotherms in the system $CaCO_3$-CO_2-0.5 M. NaCl. The data are for optical calcite.

decreased solubility of CO_2 with increasing temperature. However, as shown in figure 7, the CO_2-iso-concentration curves also have negative slopes.

Twenty-three determinations of solubility of optical calcite in 0.5 M. NaCl solution were made, through temperatures ranging from 25° to 104° and CO_2 pressures ranging from 1 to 50 bars, with the results shown in table 7, and summarized in figures 8 and 9. Solubility measurements at 25° and 100 bars could not be made due to formation of the hydrate.

TABLE 7

Solubility of optical calcite in 0.5 M. NaCl solution and CO_2.

Temperature °C.	Solubility (g/l)	Temperature °C.	Solubility (g/l)
	P_{CO_2} = 1 bar		
43	0.95	99	0.44
61	.73	99	.41
70	.60	104	.31
	P_{CO_2} = 10 bars		
24	2.43	70	1.28
42	1.87	96	0.89
42	1.90	104	.76
	P_{CO_2} = 20 bars		
24	2.91	61	1.79
42	2.28	104	0.88
	P_{CO_2} = 50 bars		
24	3.59	61	2.27
42	2.83	104	1.15
	P_{CO_2} = 100 bars		
42	3.53	104	1.35
61	2.73		

Results for 28 determinations of solubility of optical calcite in sea water through a temperature range of 23 - 96° and CO_2-pressure range of 1-10 bars are given in table 8 and figure 10.

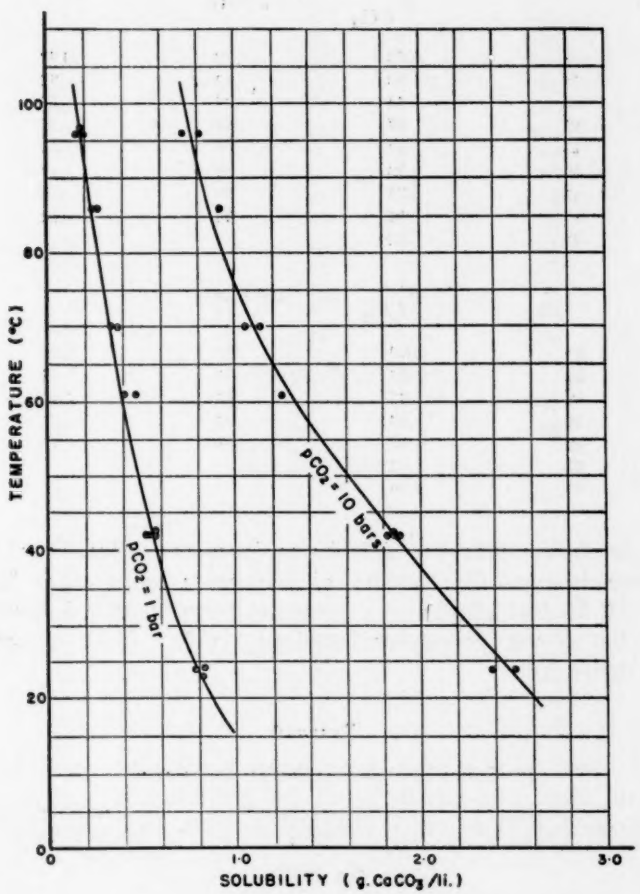

Fig. 10. Isobars in the system $CaCO_3$-CO_2-sea water. The data are for optical calcite.

TABLE 8

Solubility of optical calcite in sea water.

Temperature (°C.)	Solubility (g. $CaCO_3$/l.)	Temperature (°C.)	Solubility (g. $CaCO_3$/l.)
	P_{CO_2} = 1 bar		
23	0.82	70	0.37
24	.78	70	.33
24	.83	86	.26
42	.57	86	.23
42	.57	96	.15
42	.52	96	.17
42	.53	96	.17
61	.40	96	.18
61	.46		
	P_{CO_2} = 10 bars		
24	2.50	70	1.05
24	2.38	70	1.13
42	1.86	86	0.92
42	1.89	96	.81
42	1.86	96	.72
42	1.82		
61	1.25		

Solubility data for Solenhofen limestone.—Results of 33 determinations of solubility of Solenhofen limestone in H_2O, in 0.5 M. NaCl, and in sea water are given in table 9. Isobars in the system Solenhofen limestone - CO_2 - H_2O are given in figure 11.

TABLE 9

Solubility of Solenhofen limestone.

Temperature (°C.)	CO_2-pressure (bars)	Solubility (g. $CaCO_3$/l.)
	In H_2O	
0	1	1.48
0	1	1.48
0	1	1.45
23	1	0.98
42	1	.64
70	1	.39

TABLE 9 (Continued)

Solubility of Solenhofen limestone.

Temperature (°C.)	CO_2-pressure (bars)	Solubility (g. $CaCO_3$/l.)
	In H_2O	
0	10	2.62
0	10	2.62
0	10	2.63
24	10	2.00
25	10	1.94
42	10	1.47
42	10	1.50
42	10	1.49
42	10	1.47
70	10	0.88
78	10	.78
78	10	.76
102	10	.55
78	100	1.30
102	100	0.95
	In 0.5 M. NaCl solution	
70	1	0.66
70	10	1.36
	In sea water	
42	1	0.49
70	1	.28
96	1	.17
25	10	2.80
42	10	2.17
42	10	2.22
61	10	1.62
61	10	1.64
86	10	1.06
86	10	1.09

Solubility data for Venus mercenaria shells.—Eleven determinations of solubility of *Venus mercenaria* shells were made in CO_2 and H_2O and in sea water, with the results shown in table 10.

DISCUSSION

Of all the data that have been compiled on the solubility of $CaCO_3$, only the work of Cossa, Schloesing, Engel, McCoy and Smith, Cavazzi, Bäckström, Mitchell, Haehnel, and Frear

TABLE 10

Solubility of *Venus mercenaria* shells.

Temperature	CO_2-pressure	Solubility (g. $CaCO_3$/l.)
	In H_2O	
23	10.0	2.89
42	10.0	1.89
70	10.0	1.10
25	20.0	3.38
42	20.0	2.62
70	20.0	1.56
	In sea water	
42	1.0	0.61
70	1.0	0.31
42	10.0	2.72
61	10.0	2.02
86	10.0	1.28

and Johnston covers temperature and CO_2-pressure ranges which overlap the current work. In figure 12A, 12B, and 12C, the results of earlier work on solubility of $CaCO_3$ in H_2O and CO_2 are compared graphically with results of the present investigation.

It will be noted that the values obtained in the older investigations are in general somewhat higher than those for the current research. This discrepancy is probably due to differences in techniques and materials (especially $CaCO_3$) used for determinations of solubility.

When a solution is in equilibrium with a solid at a given temperature the solution is said to be saturated and the concentration of the saturated solution is called the solubility of the substance at this temperature. It is a well-known fact that the solubility of solids is somewhat dependent on their state of division (Hulett, 1905). Smaller particles not only dissolve more rapidly, but have a greater solubility. Bäckström (1921) has shown that the limit below which particle size has an effect on the measured solubility of aragonite and calcite is of the order of 2μ.

Practically all earlier investigators of $CaCO_3$ solubility have followed the standard practice of using finely divided material, in which case the $CaCO_3$ content of the solvent is

determined by standard methods of analytical chemistry. This may help to explain the differences in solubility values obtained (fig. 12), because $CaCO_3$ of small particle size would have a higher surface energy and hence a high equilibrium solubility. In other cases, the differences may be due to disagreement between various workers as to proper analytical procedure. This is especially true for experimental work in which very small solubility values are involved. Still another cause for differences in the values obtained by various workers is

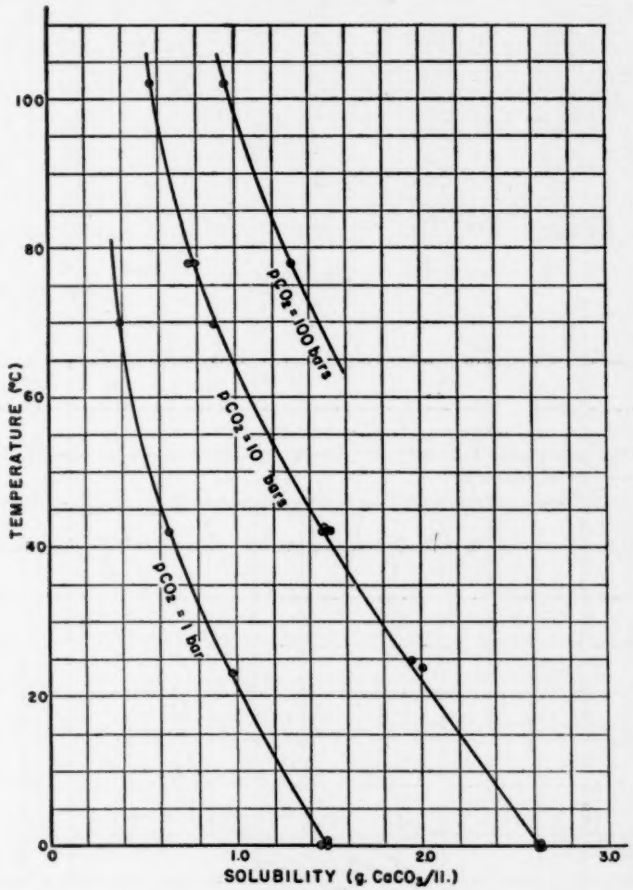

Fig. 11. Isobars in the system Solenhofen limestone-CO_2-H_2O.

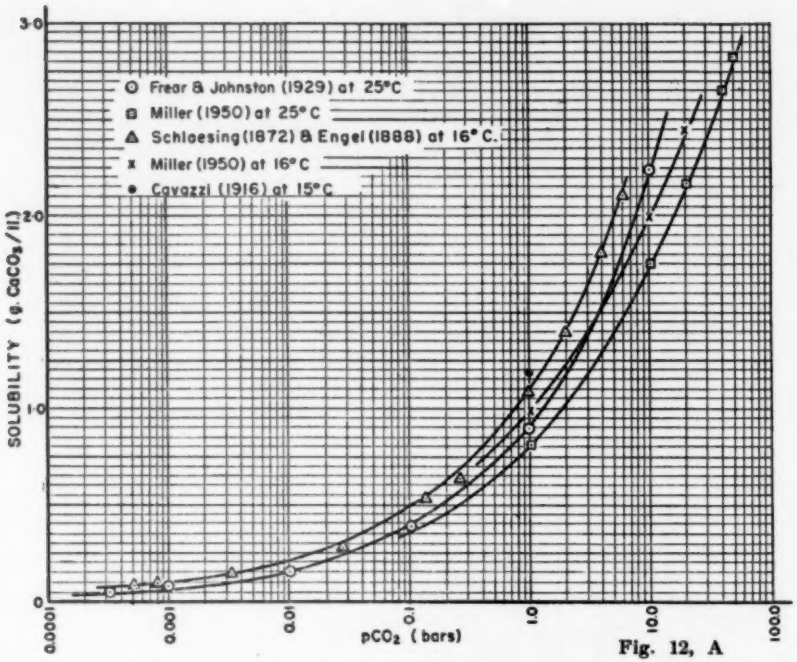

Fig. 12, A

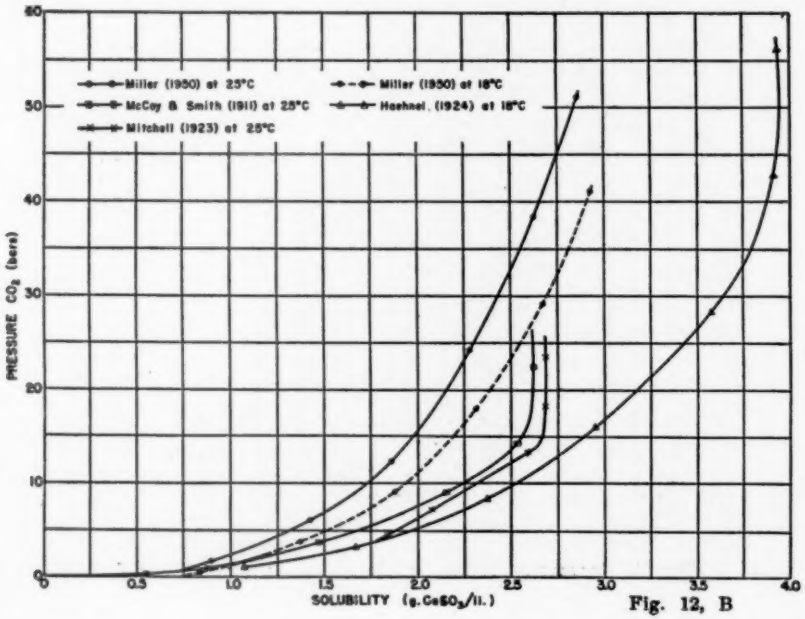

Fig. 12, B

the wide range of $CaCO_3$ materials of varying purity available for use in measurement of solubility.

Comparison of the solubility data given in this paper for Solenhofen limestone with those for optical calcite show Solen-

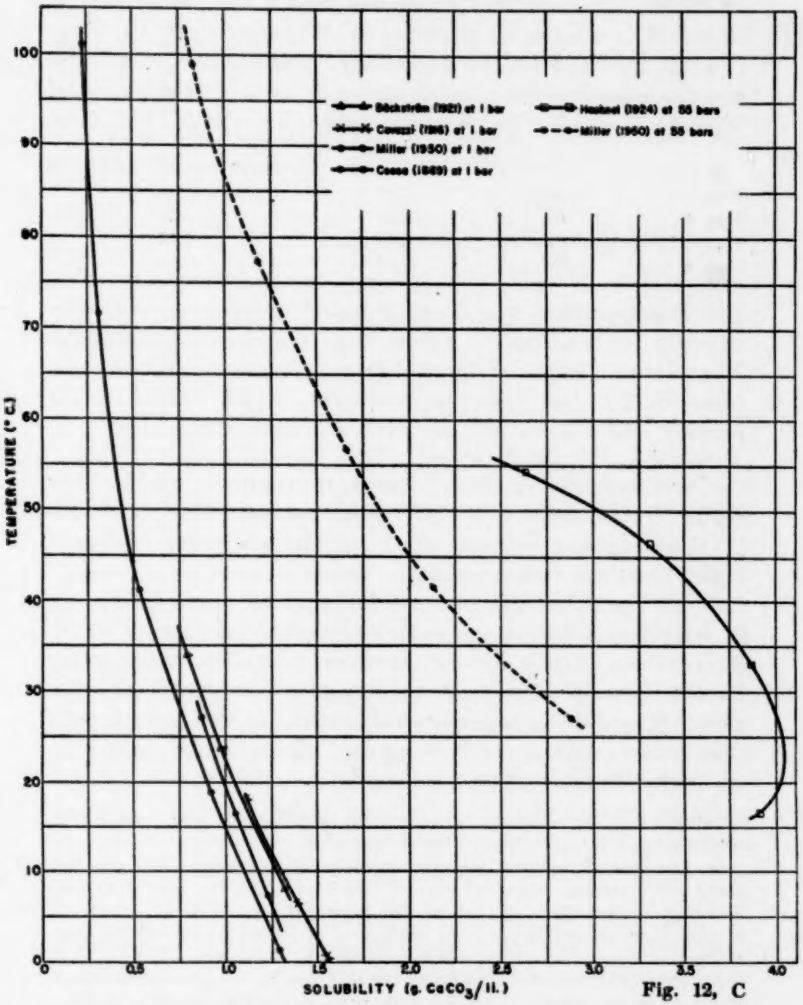

Fig. 12, C

Fig. 12. Graphic comparison of data obtained in the current investigation with results of earlier investigations. Data are for solubility in pure H_2O.

hofen to be appreciably more soluble. It was presumed that this difference was due to the greater surface of the Solenhofen material due to its extremely fine-grained texture. To test this hypothesis, determinations of solubility were made on Solenhofen limestone which had been subjected to several thousand atmospheres pressure in the laboratory of Prof. Francis Birch, Harvard University. The values given below are the result of four runs, all made at a CO_2-pressure of 10 bars. Solubility is given as grams of $CaCO_3$ per liter.

	Temperature	Solenhofen	Pressure treated Solenhofen
Run 1	42°C.	1.47	1.32
Run 2	42°	1.56	1.38
Run 3	78°	0.78	0.56
Run 4	78°	0.76	0.55

The limestone that had been subjected to pressure gave consistently lower solubility values than the untreated material. The probable explanation is that some recrystallization took place during the pressure treatment, which increased the particle size and resulted in lower solubility values.

Venus mercenaria shells proved to be more soluble than either optical calcite or Solenhofen limestone. This is due to the aragonite content of the shells, aragonite having a higher solubility than calcite.

It will be noted that the solubility of all forms of $CaCO_3$ in salt solution and in sea water is greater than in pure water. This is true despite the fact that less CO_2 dissolves in water containing salts. Previous workers have observed this same effect. The greater solubility of $CaCO_3$ in salt solutions is presumed to be due to "salting in" effects, as explained by the Debye-Hückel (1923) theory.[6]

[6] The increase in solubility produced by addition of other electrolytes which do not have a common ion is explained as follows:

In a saturated solution there is a dynamic equilibrium between ions going into solution from the crystal and ions returning to the crystal. Addition of electrolytes to the solution does not affect the rate of escape of ions from the crystal, but the number of collisions on the crystal from solution is decreased by the addition of ionized substances (because each ion is drawn in toward the body of the solution by interionic attraction). Thus, a greater total concentration is required in the presence of extra ions to give an effective concentration sufficient to maintain equilibrium conditions with the crystal. Consequently, the analytically determined solublity is increased.

Calculation of equilibrium constants.—It was found that by calculating equilibrium constants for the reaction through the range of CO_2-pressures investigated experimentally, extrapolation of the experimental data for solubility of $CaCO_3$ to low CO_2-pressures was possible insofar as data for CO_2-solubility were available. For the reaction

$$\underset{(s)}{CaCO_3} + \underset{(g)}{CO_2} + \underset{(l)}{H_2O} \rightleftharpoons \underset{(ionized)}{Ca(HCO_3)_2}$$

the equilibrium constant K at any temperature and CO_2-pressure is defined as

$$K_{t,P_{CO_2}} = \frac{[Ca(HCO_3)_2]}{[CaCO_3]\ [CO_2]\ [H_2O]}$$

where concentrations are given in moles/liter. As both $CaCO_3$ and H_2O are present in excess, each may be assigned a value of unity. Then

$$K_{t,P_{CO_2}} = \frac{[Ca(HCO_3)_2]}{[CO_2]}$$

Equilibrium constants were calculated at 25° for several CO_2-pressures, using the CO_2-solubility data of Wiebe and Gaddy (1939, 1940) and the data for solubility of $CaCO_3$ (optical calcite) determined in the present investigation. The results are plotted in figure 13. Extrapolation of the linear curve to atmospheric partial pressures of CO_2 gives values of K which closely approximate values of K calculated by using the CO_2-solubility data of Kendall (1916) and the data for solubility of $CaCO_3$ given by Frear and Johnston (1929) and Kendall (1916). From this curve the solubility of $CaCO_3$ at 25° can be calculated for any CO_2-pressure from 0.0001 to 50 bars (at pressures greater than 50 bars the CO_2-hydrate forms). Solubility values for $CaCO_3$ thus calculated compare favorably with those determined experimentally or calculated by previous investigators. For example, at $P_{CO_2} = 0.1$ bar, the calculated value is 0.37 g./li. as compared with 0.39 g./li. obtained by Frear and Johnston (1929). Under atmospheric conditions ($P_{CO_2} = 3.5 \times 10^{-4}$ bars) the calculated value is 0.044 g./li. as compared with Kendall's (1912) result of 0.046 g./li.

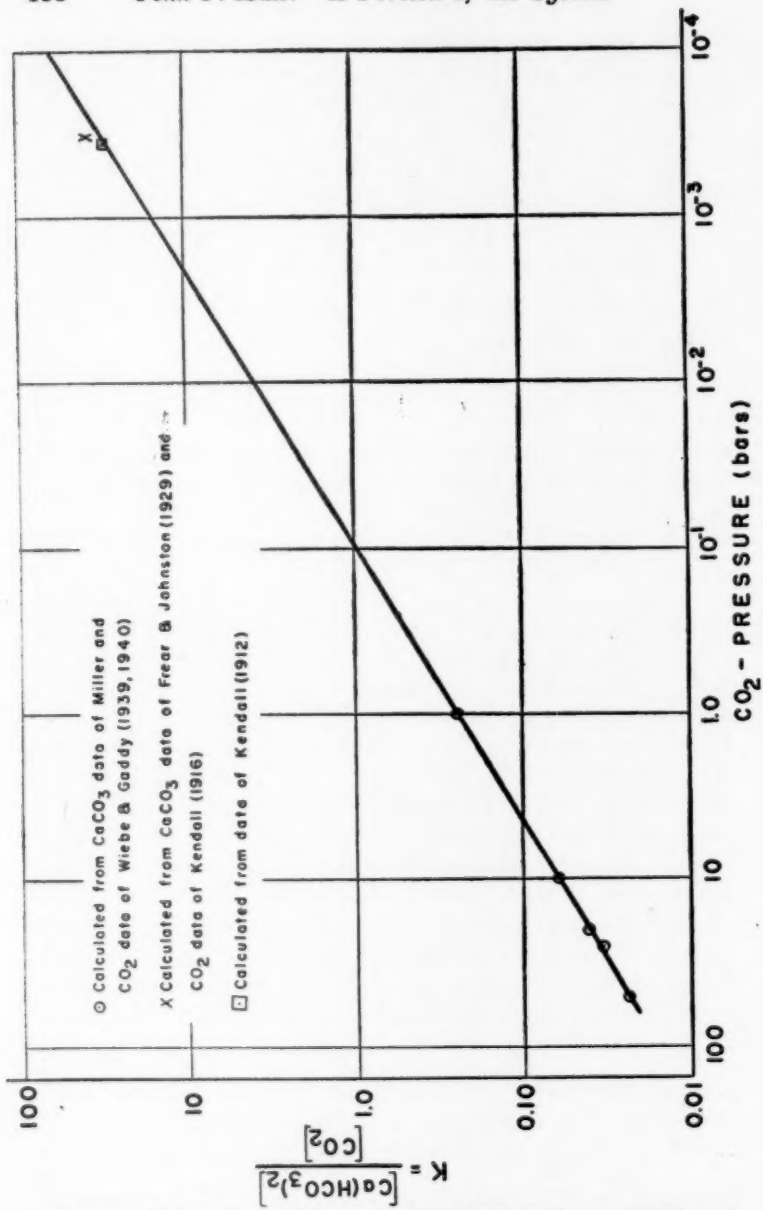

Fig. 13. Plot of the equilibrium constant K at 25°C. as a function of CO_2 pressure.

Calculation of equilibrium constants at other temperatures and extrapolation of data for solubility of $CaCO_3$ to lower CO_2-pressures were not possible due to lack of CO_2-solubility data in the low CO_2-pressure range.

The data for the solubility of $CaCO_3$ (optical calcite) experimentally determined or calculated in the present investigation were plotted on a three-dimensional diagram, shown in figure 14. In addition, the value of Kendall (1912) for solubility at $P_{CO_2} = 3.6 \times 10^{-4}$ bars and 100°, and the result of Wells' (1915) determination of solubility at $P_{CO_2} = 3.0 \times 10^{-4}$ bars and 0° were plotted. Isotherms were drawn at 25° intervals and CO_2-isobars at 100, 10, 1, etc. bars. The data thus plotted form a surface representing the system $CaCO_3$-CO_2-H_2O through temperatures ranging from 0° to 100° C. and CO_2-pressures ranging from 3.5×10^{-4} to 100 bars. It will be noted that the metastable solubility curve of calcite noted by Haehnel (1924) does not appear. At high CO_2-pressures and low temperatures the solid phase CO_2-hydrate forms and its field of stability appears on the diagram as a corner torn from the surface representing solubility of $CaCO_3$. As noted by Frear and Johnston (1929) solubility of $CaCO_3$ at 25° through CO_2-pressures ranging from 3.5×10^{-4} to 10 bars is approximately proportional to P_{CO_2}. At higher temperatures and CO_2-pressures this relationship does not hold.

Calculation of the heat of reaction.—The heat of reaction for the equilibrium

$$\underset{(s)}{CaCO_3} + \underset{(g)}{CO_2} + \underset{(l)}{H_2O} \rightleftharpoons \underset{(ionized)}{Ca(HCO_3)_2}$$

is given by the following relationship:

$$\Delta H = -\ln K R T$$

where ΔH = heat of reaction

K = equilibrium constant $\dfrac{[Ca(HCO_3)_2]}{[CO_2]}$

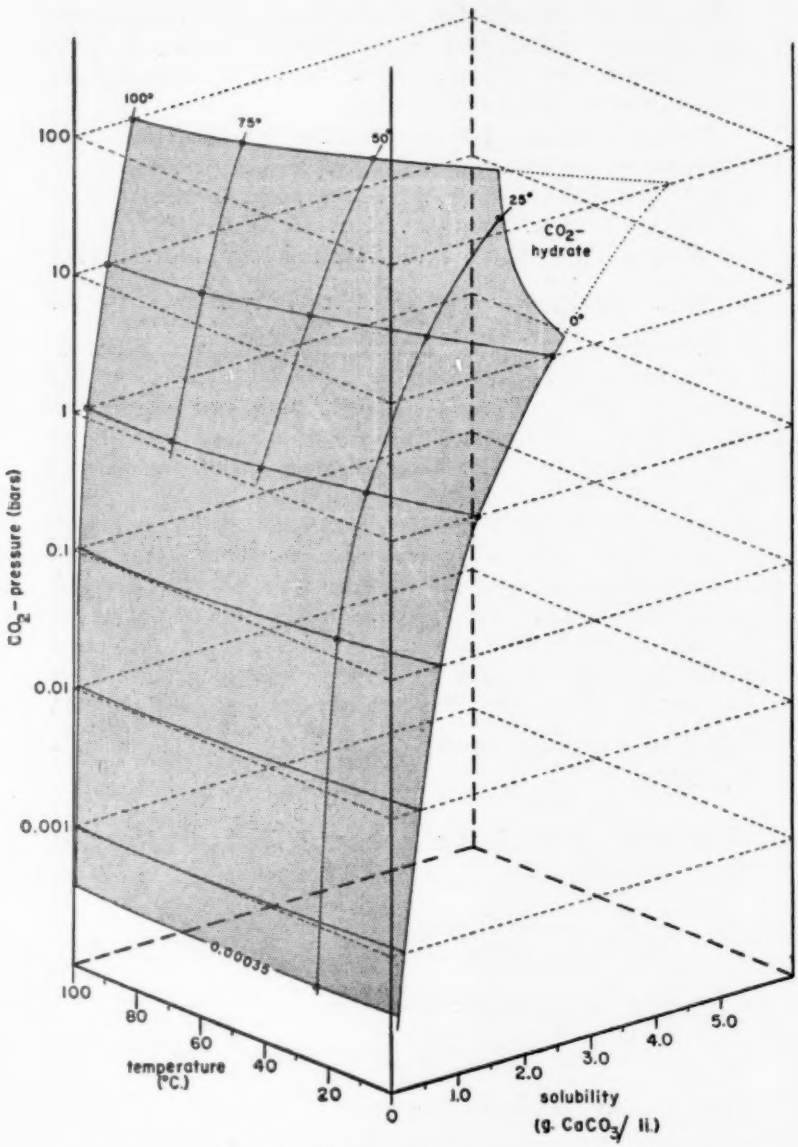

Fig. 14. The system $CaCO_3$-CO_2-H_2O for temperatures ranging from 0-100°C. and CO_2-pressures from 0.00035 - 100 bars.

The heat of reaction was calculated for four CO_2-pressures, with the results shown below.

P_{CO_2}	ΔH
100 bars	− 2.60 kg.-cal./mole
75	− 2.41
50	− 2.08
25	− 1.38

No values for ΔH were found in the literature for comparison.

Accuracy of present work.—The accuracy of laboratory operations (measurement of CO_2-pressure, temperature, etc.) involved in determination of solubility was discussed in the sections on *apparatus* and *experimental procedure.*

In figure 4, it will be noted that the isobars are curves representing mean values drawn through points which show a considerable spread. The points on either side of the isobars deviate from the curve drawn by as much as 10% in a few cases. The mean deviation of points is 2.6% for the 1-bar curve and 1.0% for the 100-bar curve. Approximately the same degree of deviation prevails in the data shown in figures 8, 10, and 11.

Attempts to improve the consistency of the data were unsuccessful, and the exact cause of the spread of values is still unknown. Several possibilities are considered.

Figure 3 seems to show that equilibrium was attained under the present experimental conditions. Stirring the solution would have probably shortened the time required for attainment of equilibrium, but no technique for stirring in the bombs was available.

Differential solubility on the various crystal faces is known to occur, but as all the plates of optical calcite used in these experiments were cleavage fragments, errors from this source should be negligible. Also, if this effect were of major significance, experiments with Solenhofen limestone, in which crystal faces are apparently randomly oriented, should have produced highly consistent data. This was not the case.

Perhaps the most questionable part of the procedure was the final stage of each run, when the bombs were removed from the furnaces (thereby suddenly lowering the temperature) and immediately unsealed (thereby suddenly decreasing the

CO_2-pressure). This technique could conceivably result in some recrystallization back onto the calcite plates, and the solubility values would thereby be lowered. It was noted, however, that precipitation of $CaCO_3$ from the water in which the runs were made apparently did not begin until several minutes after the plates were removed, at which time a very fine white powder appeared in the liquid. If recrystallization back onto the plates were appreciable, it seems unlikely that determinations of solubility involving plates of various sizes and weights would give the consistency actually obtained. Also, if this effect were of major importance, it seems that data for solubility at low temperatures and CO_2-pressures should show smaller deviations. This was not found to be true.

GEOLOGICAL IMPLICATIONS

The data presented in this paper are the result of the most extensive investigation of the system $CaCO_3$-CO_2-H_2O completed to date. The results show that the solubility depends not only on temperature and CO_2-pressure, but also on purity and particle size of the $CaCO_3$ and on the concentration of other ions.

Many previous investigations of solubility of $CaCO_3$ have been made using finely powdered material. In nature, $CaCO_3$ commonly occurs in rather coarsely crystalline form as massive aggregates of limestone. For this reason, the data presented in this paper may be more closely representative of natural equilibrium solubility conditions than those from previous investigations. Actually, the solubility values determined in the present work are not markedly different from those given by earlier investigators (fig. 12), though in general they are somewhat lower. Such differences as are noted no doubt reflect differences in the experimental methods used and perhaps differences in the purity or particle size of $CaCO_3$ used for determinations of solubility.

There are numerous factors of unknown magnitude which complicate any attempt to apply the experimental results for solubility of $CaCO_3$ to natural conditions. Naturally-occurring carbonates are always more or less impure. Under most natural conditions, as in the soil, the CO_2-H_2O equilibrium is only one of several means by which $CaCO_3$ may be dissolved. In any natural situation where the CO_2-H_2O equilibrium pre-

dominates in the solubility of $CaCO_3$, it is uncertain that equilibrium solubility conditions are attained.

The solubility of very pure $CaCO_3$ in H_2O and CO_2 under widely ranging conditions of temperature and CO_2-pressure can be read from figure 14. For any equilibrium involving these three substances, the conditions required to maintain a given solubility value for $CaCO_3$ can be determined. In nature, however, such a simple equilibrium as that studied experimentally in the present investigation is exceptional. Perhaps rain falling upon a limestone area comes as close to approximating the system $CaCO_3$-CO_2-H_2O as any occurring in nature. Assuming the rain to be in equilibrium with an atmospheric partial pressure of CO_2 (3.5×10^{-4} bars) and to contain no impurities, rain water could dissolve 0.044 g. $CaCO_3$ per liter at 25° C. This would mean that 3.1 tons of $CaCO_3$ per square mile per inch of rain could be removed from the limestone area, provided equilibrium in the system $CaCO_3$-CO_2-H_2O was attained and provided the $CaCO_3$ once dissolved was not reprecipitated. Under humid conditions (assuming a rainfall of 40 inches per year), reduction of the area would proceed at the rate of one foot in 11,100 years. Under arid conditions (assuming an annual rainfall of 10 inches), the rate of lowering of the land surface would be one foot in 44,700 years. From his study of the salt content of natural waters, Reade (see Clarke, 1924) estimates that the level of England and Wales is being lowered at the rate of one foot in 12,978 years by the solvent action of water alone. Clarke (1924) estimates the United States, exclusive of the Great Basin, is being lowered at the rate of one foot in 23,984 years due solely to solvent denudation. As he points out, reduction of limestone areas would proceed much more rapidly than the average rate for all types of rocks.

Water at 0° C. and in equilibrium with an atmospheric partial pressure of CO_2 would be capable of dissolving 0.081 g. $CaCO_3$ per liter, or nearly twice as much as rain at 25°. Williams (1949) has suggested that solution by melt-water from snow banks plays an important role in nivation. Though the information he presents is of interest, it appears that he does not place sufficient emphasis on the mechanical aspects of nivation, especially comminution by frost action and transportation by flowing water.

Ground water is much more complex chemically than rain water or snow, due to the presence of organic acids, colloids, and inorganic ions acquired during percolation through soil and rock. Most ground water contains less than 200 parts per million of $CaCO_3$ (0.20 g./li.), though in some cases as much as 400 parts per million may be present. From diagram 14 it is found that a CO_2-pressure of 0.107 bars is required to maintain 400 parts per million of $CaCO_3$ in solution at 25° C. This is a CO_2-pressure 300 times greater than that prevailing in the atmosphere. In terms of the equilibrium between $CaCO_3$-ground water-atmospheric CO_2, water containing such a quantity of $CaCO_3$ would be supersaturated. However, ground water is affected by certain processes which tend to increase the solvent capacity of the water for $CaCO_3$. According to Adams and Swinnerton (1937) the air of soil deficient in humus contains 25 times as much CO_2 as atmospheric air and the ratio may be increased to more than 100 if organic matter is supplied to the soil. They point out that the maximum measured partial pressure of CO_2 in soil air was 0.0974 atmospheres, but that it is believed that in India under conditions of poor ventilation (during the monsoon) soil air may contain 16-20% CO_2. In addition to enrichment of CO_2, there are the "salting in" effects of inorganic ions and the presence of "humic acids", both factors which are difficult to evaluate quantitatively at the present state of knowledge. The general tendency of each of these factors would be to make ground water a better solvent for $CaCO_3$ than water in equilibrium with an atmospheric partial pressure of CO_2.

Carbonic acid is considered to be the most important acid in weathering processes. By reaction with H_2CO_3, calcium in rocks of all types may be dissolved and transported in solution. As suggested above, weathering processes are so complex and so poorly understood that discussion of the chemical breakdown of rocks in light of the data obtained in the present investigation is impossible at this time.

Though most limestones are considered to be due primarily to organic processes, there are certain inorganic factors which may have been of considerable importance. Johnston and Williamson (1915, 1916b) pointed out that the surface layers of the warm portions of the oceans are saturated with $CaCO_3$. They reasoned that increased temperatures would result in

supersaturation due to loss of CO_2 and that some $CaCO_3$ would be precipitated by this means. They presented experimental and calculated data to show the effect of changes in temperature and CO_2-pressure on solubility of $CaCO_3$. The few determinations of solubility of $CaCO_3$ in sea water made during the current investigations are not adequate for any conclusions on the question of inorganically precipitated limestones. The values given for solubility of $CaCO_3$ in sea water at $P_{CO_2} = 1$ bar are probably applicable to solution of $CaCO_3$ under conditions of poor aeration in the ocean.

As for so many simple laboratory experiments direct application of the data obtained in this investigation to natural processes is not feasible at the present state of knowledge. Yet there is value to making such studies in that the only way to unravel the complexities of nature is to study small segments of it at a time and from the small segments build up a composite picture. The data presented in this paper, though as precise as careful technique can make them, include too few components of natural systems to permit drawing any far-reaching conclusions regarding the nature and rates of geologic processes.

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ICE-RIDGED MORAINES AND THEIR RELATION TO GLACIERS

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ABSTRACT. "Fluted" surfaces of moraines from which glaciers have recently retreated are due mainly to the presence of parallel ridges representing the fillings of subglacial tunnels which form in lee of boulders. Weight of overlying ice forces material upward into the tunnel making a ridge, so that the moraine surface is a cast of the grooved base of the ice. In some cases tunnel formation occurs beneath actively moving ice with a thickness greater than 200 feet.

INTRODUCTION

ADJACENT to most Montana glaciers, especially Grinnell and Sperry in Glacier National Park, overridden moraines from which the ice has recently retreated are marked with conspicuous ridges paralleling the direction of ice movement. Where closely spaced they give the surface of the moraine a fluted appearance (plate 1, fig. 1). Most ridges are from 2 to 12 feet wide and from 1 to 3 feet high. Some have lengths of 500 to 600 feet. Although width does not vary throughout the length of the ridge, height in most cases diminishes gradually, almost imperceptibly, in the direction away from the glacier. Toward the glacier most ridges which do not disappear under the ice terminate against a boulder lying on, or partially embedded in, the moraine. In practically all cases the upstream and top surfaces of such boulders, especially the larger ones, have been striated and worn smooth by debris in the ice which formerly overrode them. As a result they have a sort of roche moutonnée form (plate 1, fig. 2). Material in the ridges is similar to that in adjacent parts of the moraine except that there is a higher proportion of finer material and rock flour immediately in lee of many of the larger boulders. The conclusion that the ridges result from complete or partial filling of tunnels which form in basal ice in lee of boulders as the glacier moves over them seems justified.

Inasmuch as ridges of this type have been exposed for a comparatively short period, the length of time over which they might persist as visible features is not known. Adjacent to Jackson Glacier in Glacier National Park ridges exposed fifty or more years ago are still discernible, although par-

tially covered with small willows and other vegetation. In places the presence of the ridges is indicated by the alignment of this vegetation.

Rapid glacier shrinkage of recent years has exposed so many of these ridges to view that it is felt they deserve more attention than they have received in the past. Further, their study may shed some light on the critical and important problems of glacier mechanics.

The writer first examined such ridges in Glacier National Park, Montana, between 1935 and 1940. Similar ridged moraines, however, were noted about fifty years ago adjacent to the Columbia Glacier in Alaska (Gilbert, 1910, pp. 77-78), and subsequently at other Alaskan glaciers. At Petrof Glacier in 1909 Grant and Higgins (1913, p. 66 and plate XL) found them to be 1 to 5 feet wide and 6 to 18 inches high and extending out from the ice front with lengths as great as 200 feet. Although their photograph shows the ridges to be straight and regular, the authors state that they form as the result of debris falling into fissures near the ice front. At Mendenhall Glacier, Ray (1935, pp. 310-311) found them well developed over an area of several hundred square yards on a gravel outwash plain. He suggested that they are formed by grooving of the gravel when the cuspate undersurface of the ice passes over it, and further that some are formed in lee of cobbles which impress their form into the ice, as had earlier been inferred by Gilbert (p. 78), who found such features on moraine, and not on outwash as had Ray. Because of the relation of ridges to the boulders it would appear, however, that the undersurface of ice in motion is not cuspate, but grooved.

At Woodworth and Schwan Glaciers in the Tasnuna Valley and at Heney Glacier in the Copper River Valley of southeastern Alaska, Bradford Washburn has photographed similar ridges (plate 2) from the air. Tarr and Martin (1914, pp. 448-449 and plate CLXXX) had previously noted and photographed those at Heney Glacier. Washburn's photograph at Woodworth Glacier shows that the ridges, some of which are 1,100 feet long, completely cover a surface of drift from which the glacier had recently retreated. The ridged area was several hundred acres in extent when the photograph was taken. Near the ice front and elsewhere on the debris surface are several boulders with ridges in their lee (plate 2). Most

of the large boulders in lee of which there are no ridges probably were dropped from within the ice or from its surface.

Where the terminal portions of glaciers rest upon rock floors, tunnels formed by bedrock obstructions emerge at the ice front. Because of the absence of debris it is possible to enter these tunnels and proceed in some cases as far as the rock obstruction. Alden (1914, p. 15) found such caves at Sperry Glacier from 50 to 100 feet long which were fluted in correspondence with irregularities of the surface over which the ice passed. More recently Carol (1947) penetrated tunnels leading from marginal crevasses in the upper Grindelwald Glacier more than 150 feet below the glacier surface, proving that even at that depth ice in passing over an obstruction does not immediately re-conform to the shape of the rock floor. Although his observations were made along the glacier margin Carol (1945, pp. 44-45; 1947, pp. 58-59) found that ice, forced against the upstream side of an obstruction, lost its rigidity and became plastic.

Inasmuch as some of the tunnel ridges at Sperry and Grinnell Glaciers extend to the crest of the modern moraines, it has been possible, aided by photographs, to reconstruct the longitudinal surface profiles of the glaciers and thus to determine the former maximum thickness of the ice over the boulders and the ridges in their lee (fig. 1). At Sperry Glacier ice overriding several of the tunnel-forming boulders apparently was at least 240 to 260 feet thick. At Woodworth Glacier (plate 2) the thickness may have been considerably greater. The failure of basal ice to fill the space in lee of these boulders shows that it possessed considerable strength, even though locally exhibiting plastic flow (at upstream face of boulder). Thus it would appear that openings, even in an actively moving glacier, may be present at depths considerably greater than 150 feet which, according to Demorest (1938), is the minimum depth necessary to cause ice to flow dominantly according to the laws of fluid mechanics, and below which hydrostatic pressure presumably is sufficient to prevent the formation of open fractures and cavities. Furthermore, Carol (1945, p. 50) has actually penetrated the Upper Grindelwald Glacier to a depth of 72 meters through meltwater tunnels which presumably continued to much greater depth.

ORIGIN OF THE RIDGES

Although the origin of tunnels in basal ice has been ably discussed by Carol (1945 and 1947) and others, the type of ridge described herein has received less attention. Because it

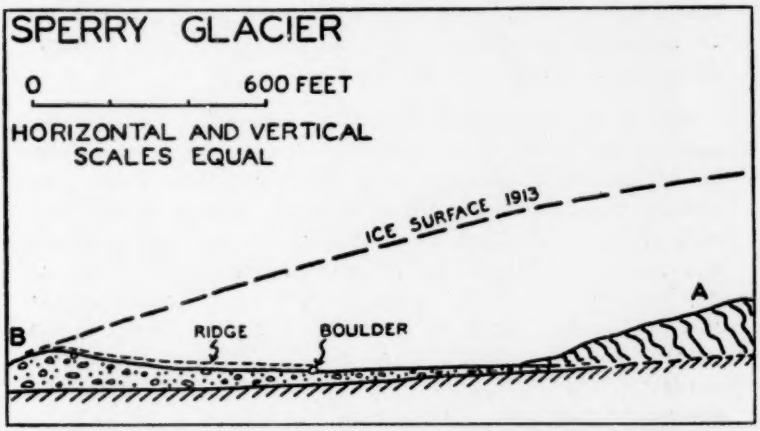


Fig. 1. Section at front of Sperry Glacier along the line A-B (fig. 2). The 1913 ice surface is based largely upon photographs by W. C. Alden. Height of tunnel-fill ridge is exaggerated.

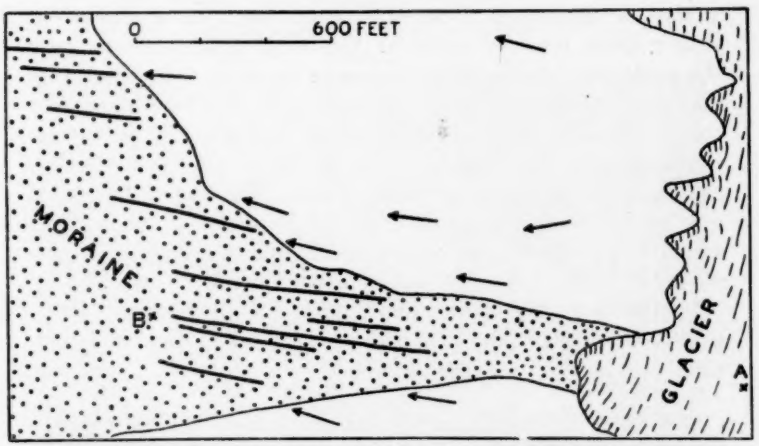


Fig. 2. Map of an area at the front of Sperry Glacier in 1946 showing principal tunnel-fill ridges (heavy lines on moraine) and striae. Blank areas are bedrock.

reflects a condition of the ice in a place where observation is difficult, if not impossible, this discussion is presented.

There are several means by which such ridges may have been formed: (1) direct deposition from the ice; (2) erosion or pushing forward of material not in lee of boulders; (3) squeezing of debris up into the tunnel by weight of the ice on the moraine, especially where much rock flour is present; or (4) a combination of the above.

Direct deposition from the ice.—If material in the ridge accumulated in this manner, the latter would not have uniform height and width. The ice would yield debris only by melting with resultant increase in the diameter of the tunnel, especially with distance from the boulder. A small quantity of debris apparently accumulates in this manner immediately in lee of the boulder where it is squeezed from ice deflected by the obstruction, but complete or nearly complete filling of the tunnel obviously is out of the question. Further, the ineffectiveness of this method of formation is attested to by the absence of tunnel-fill ridges lying on bedrock surfaces.

Erosion of moraine surface.—Ridge formation is probably due in part to this process although the presence of tunnel-fill ridges in lee of small boulders and even cobbles (less than 1 foot in diameter) is an indication that the ice overrode rather than removed some of the very small obstacles. On the surface of the Grinnell Glacier moraine most boulders with diameters greater than 2 feet are striated mainly, if not solely, on their upstream sides indicating that they were overridden by the ice. Thus the last movement of the ice (when the tunnels were still forming) before the glacier retreated was hardly capable of eroding flutes (channels) in the moraine surface. The flowing of ice around small loose obstacles was observed under the edge of the Aletsch Glacier in 1876 by Niles (1878, p. 367) and several years later by Spencer (1887, pp. 168, 169) in Norway. The ice at both places was very thin, but it was in motion.

Squeezing debris into tunnel.—If unfrozen, drift underneath terminal portions of temperate glaciers is saturated with water which descends from the surface or forms by pressure-melting at that depth. Under such wet conditions the debris

PLATE 1

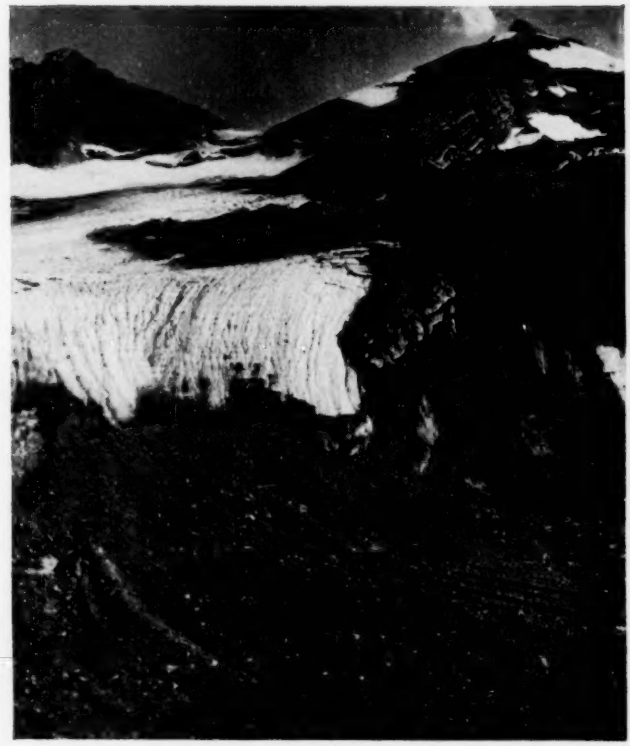


Fig. 1. Ridged moraine at front of Sperry Glacier.

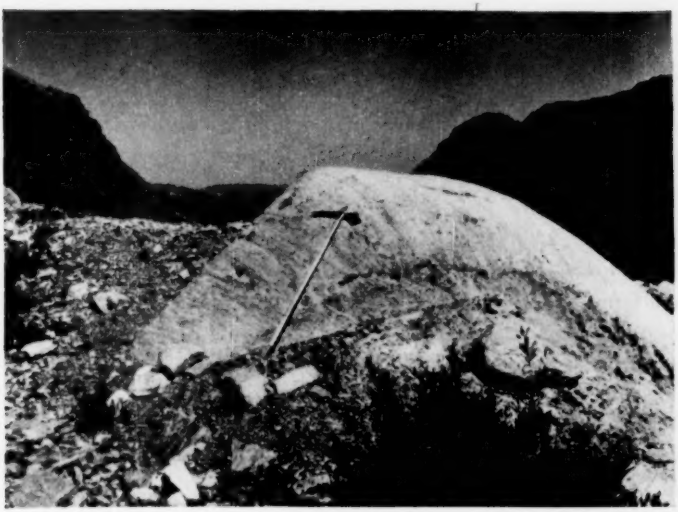
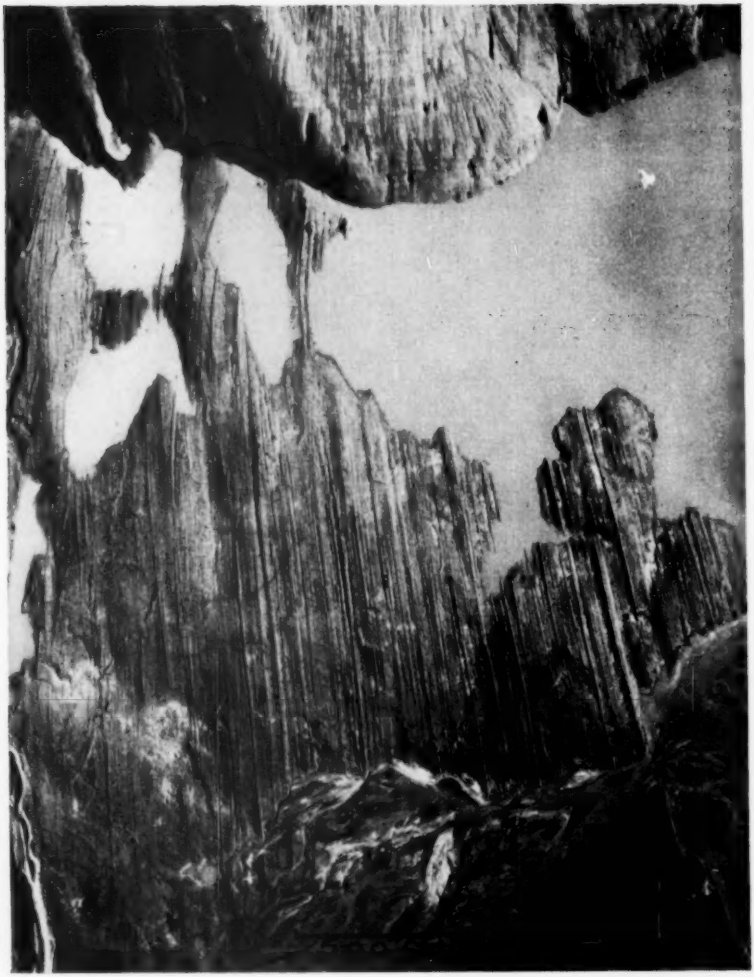


Fig. 2. Ridge-forming boulder on moraine at Grinnell Glacier. The tunnel-fill ridge is at the left beyond the boulder.

PLATE 2



Ridged surface of debris at front of Woodworth Glacier, Tasnuna Valley, Alaska. The length of scale line is 500 feet. Photograph by Bradford Washburn.

possesses a plasticity which presumably would enable it to conform, under the weight of overlying ice, to irregularities in the undersurface of the glacier.

In Glacier National Park the largest and most pronounced ridges occur on moraine which contains a relatively high proportion of rock flour, although ridges are present on all types of morainic material. On the older moraines it is probable that much of the rock flour, present when the ridges were formed, has been removed.

It seems unlikely that the ridges formed on frozen drift. Observations in Glacier National Park have disclosed that nowhere along the fronts of the glaciers there or at the bottoms of terminal crevasses is the moraine frozen between early June and late September. The last great advance of these glaciers, a time when they might conceivably have encroached upon a frozen drift surface, took place prior to 1850 (Matthes, 1940, p. 400), but the climatic change responsible for this advance, although evidenced by the increased accumulation of ice, could hardly have been of sufficient magnitude to have created a permanently frozen surface adjacent to the glaciers.

At present moraine underlying terminal parts of Sperry and Grinnell Glaciers is very wet and unstable during the summer months. In walking on the surface of this material along the glacier margins one is apt to sink to his knees, and where rock flour is abundant, can extricate himself with difficulty.

On an area of about two acres near the terminus of Grinnell Glacier are several parallel "push ridges" made by the advancing ice front plowing into the moraine. Their maximum height generally is about one foot. Even though rapid recession has been in progress for many years there are brief intervals, probably in late winter or early spring, when the terminus moves a short distance forward. Any such annual advances, however, in the Glacier National Park area have for many years been much less than the subsequent summer recession. Push ridges (push moraines) for most years between 1935 and 1946 are discernible at Grinnell Glacier. These ridges might be regarded as evidence that the undersurface of the glacier pushes debris forward and therefore that the tunnel-fill ridges are remnants preserved in lee of boulders, whereas the remainder of the moraine surface, not so protected, has been eroded away. On the other hand, there is no

evidence that debris is being moved forward anywhere except at the advancing ice edge. Push ridges are best developed where the ice front is moving against the steep reverse slope of a moraine, or where it lies on a mass of well-saturated moraine in which the clayey matrix is quite plastic. In the latter case some of the material is squeezed from underneath the ice edge.

Formation by more than one process.—It is possible that the ridges owe their origin to more than one of the foregoing processes, although it would appear that squeezing of material into the tunnel by weight of the ice is most important.

SIGNIFICANCE OF THE RIDGES

Ridged moraine surfaces which have been variously described as furrowed, ridged and furrowed, fluted, and even striated (Chamberlin, 1940, p. 53), are marked largely by ridges which are fillings of subglacial tunnels in lee of boulders over which ice formerly moved.

The abundance of subglacial tunnels bears out the belief that thinning of terminal portions of glaciers is aided appreciably by basal ablation where the ice coming into contact with the upstream side of an obstruction is melted because of increased pressure.

Actively moving ice, 200 or more feet thick, under certain conditions apparently is incapable of moving small boulders lying on the rough surface of the moraine, or partially embedded in it.

On the other hand, ice which seems to be incapable of removing morainic obstructions, or of extricating individual boulders, apparently is able to abrade bedrock surfaces with rock fragments previously incorporated within the ice. At both Sperry (fig. 2) and Grinnell Glaciers the alignment of tunnel-fill ridges parallels the striations on adjacent bedrock in such a manner that it is evident subglacial tunnels were being formed while nearby ice, with essentially the same thickness, was striating and grooving bedrock.

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POLLEN ANALYSIS OF THE HORRY CLAY AND A SEASIDE PEAT DEPOSIT NEAR MYRTLE BEACH, S. C. *

DAVID G. FREY

ABSTRACT. The Horry clay below the section described by Cooke is a freshwater deposit. Deposition of the middle portion of this formation was attended by climatic conditions evidently moister, and probably also warmer, than was either the top or bottom portion. The rapidly increasing percentage of pine towards the top seems to indicate, on the basis of North Carolina experience, progressive cooling, although the entire formation was laid down during an interglacial age. This has been assumed by others to be the early part of Sangamon time, followed by the deposition of the overlying marine Pamlico formation. Nearby at Myrtle Beach State Park there is a seaside peat deposit of uncertain stratigraphic relationship to the Horry clay, although presumably younger, that dates from a glacial age. The chief evidence for this is the high percentage of spruce among the tree pollens present in the salt marsh peat. It is believed the Myrtle Beach peat is more likely Wisconsin than Illinoian in age. There is no known unconformable relationship between the Horry clay and the Pamlico formation.

INTRODUCTION

AT two known localities in the Atlantic Coastal Plain a dark carbonaceous clay containing rooted cypress stumps occurs immediately beneath the marine Pamlico formation. The first such record was reported by Holmes (1885) for a site on the southwest bank of the Neuse River 10 miles below New Bern, N. C. At this location cypress stumps up to 8 feet in diameter are visible for several hundred yards along the river, and in one place where the bank has been eroded back they occur as much as 40 yards offshore projecting out of the water.

This site was subsequently revisited by Berry (1926) who identified the cypress as *Taxodium distichum*, by Mansfield (1928) who described the geological section exposed at this site and listed the marine shells of the overlying Pamlico formation and the diatoms of the clay itself, and finally by Richards (1936) who merely confirmed many of Mansfield's observations. At stations both upstream and downstream a mile or two from this site Mansfield noted that the Pamlico rested unconformably directly upon the underlying Pliocene

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deposits, and he concluded that the cypress-containing clay was laid down in a stream cut channel.

Shortly after the Intracoastal Waterway was constructed in the middle 1930's, Cooke (1937) found a similar section along the waterway near Myrtle Beach, S. C., which he described and named the Horry clay. This deposit is overlain by 18 feet of Pamlico formation, the lower 6 feet of which are loaded with marine fossils, principally molluscs. In the 3 feet of Horry clay exposed at this site 53 species of diatoms were identified, the majority of which are marine. This contrasted sharply with the Neuse River site, where 8 out of 10 species found are freshwater diatoms, the most abundant being *Nitzschia scalaris* (Mansfield, 1928). Yet in spite of the apparent environmental differences concerning their deposition, Cooke believed the two deposits were contemporaneous, and Richards (1950) concurred.

The most abundant diatom at the Myrtle Beach site is *Polymyxus coronalis*, a marine species now extinct along the Atlantic coast of North America but still living off the mouths of the Para and Amazon rivers. This and several other diatoms of present southern distribution suggested to Cooke that the Horry clay "was deposited under conditions at least as warm as, and most probably warmer, than those existing in the same region today." Cooke concluded, therefore, that the deposit could not have been laid down during a glacial age, but was probably laid down in the early part of the interglacial age that included Pamlico time. This is most likely the Sangamon, according to Flint (1947), although it is by no means proved.

Pollen analysis of Pleistocene carbonaceous sediments is a tool that geologists in this country have not utilized so widely as they might in helping them to draw conclusions. It was therefore of considerable interest to the author to be asked by Stephen Taber to analyze the pollen of the Horry clay for the light it might shed on the conditions of temperature, moisture, and salinity during the deposition of this formation.

MATERIALS

Eight samples in the present study are from the Horry clay at the Inland Waterway site near Myrtle Beach. The other 2 samples are from the peat deposits being eroded by

TABLE 1.

General description of samples from Myrtle Beach peat and Horry clay, arranged in stratigraphic sequence.

	Sample	Distance from top of Horry clay [1]	General description
Myrtle Beach peat	Upper peat	++	Brownish-black peat, with rounded quartz grains and pebbles up to 2-3 mm. diameter throughout.
	Lower peat	+	Brownish-black peat; much less sand than in previous sample.
Horry clay	Stump sample	-	Dark-gray silty-clay, very compact and smooth; small percentage of fine sand grains.
	39-1	1'3"	Fine textured black silt, compact, with large amount of amorphous organic matter; a few small marine (?) bivalves.
	39-2	2'9"-3'3"	Black, crumbly organic sediment, with occasional small twigs or bits of wood; almost no inorganic matter.
	39-3	3'6"-3'11"	Black, crumbly organic sediment; larger quantity of plant and wood fragments than in previous sample.
	39-4	3'11"-4'4"	Dark-gray silty-clay of irregular texture; some small sand grains and a few plant fragments.
	39-5	5'2"-5'9"	Medium-gray clay, fine and smooth, compact; only occasional plant fragments.
	39-6	7'1"-7'7"	Light- to medium-gray, fine sandy-clay; mottled in appearance from fibrous plant remains.
	39-7	7'7"-8'0"	Light to medium brownish-gray sand, coarser than above but with fair amount of clay as a binder; mottled appearance from organic fragments.

[1] The top of the Horry clay is 2'0" above mean sea level. The upper peat sample is above, and the lower peat sample is below mean sea level.

the sea at Myrtle Beach State Park, 4½ miles from the Horry clay site. The peat deposits are presumably younger than the Horry clay.

Taber collected 7 samples from the Horry clay on November 14, 1949, with the aid of an earth auger. These samples are listed by field number in table 1. The other sample from the Horry clay was collected by the author on November 6, 1949, near the base of one of the cypress stumps at the same site. Its exact position in the section is not known, although on the basis of its pollen spectrum to be discussed later it is quite evidently younger than 39-1.

At Myrtle Beach State Park a sample of the peat exposed only at low spring tides was collected by the author on November 6. This sample is hereafter referred to as "lower peat".

It should be noted here that the Horry clay is considerably thicker than the 3 feet reported by Cooke. Taber was able to put the earth auger down 8 ft. 11 in. into the formation. In general the lowermost portion of the deposit consists of rather fine brownish-gray sand with organic fragments. Proceeding upwards the color gradually becomes darker, indicating an increasing percentage of organic matter, and at the same time the average particle size becomes smaller until in sample 39-2 there is virtually no inorganic matter. This trend in particle size indicates a progressive reduction in current and wave conditions, and perhaps also a reduction in amount of runoff from the nearby land. Enclosed basin sedimentation is indicated. Above sample 39-2 silt and clay again appear in quantity, and the organic content decreases.

The peat deposit at Myrtle Beach is almost entirely organic, except for occasional sand grains in the lower peat and more abundant wave-rounded sand grains and small stones in the upper peat. The material is a marsh deposit, rather than a basin deposit.

METHODS

A single method of preparing pollen slides cannot be employed for all types of deposits. Where pollen is abundant and not obscured by too much other material, it suffices merely to boil a small sample in 10% KOH to thoroughly deflocculate the particles. Where there is a preponderance of

TABLE 2.

Method of preparation of samples, and relative abundance of tree pollens in them.

	Sample	Method of preparation	Total tree pollens	Slide rows examined	Abundance factor	Condition of pollen
Myrtle Beach peat	Upper peat	KOH - acetolysis	65.5	59	1.1	well preserved
	Lower peat	KOH - acetolysis	55	44	1.3	well preserved
Horry clay	Stump sample	KOH - 3x bromoform	151	5	30.2	considerably fragmented
	39-1	KOH - 2x bromoform	81	21	3.9	poorly preserved, crumpled, fragmented
	39-2	KOH	155	15	10.3	mostly well preserved
	39-3	KOH - acetolysis	166	7	23.7	well preserved
	39-4	KOH - 2x bromoform	155	19	8.2	surface obscured, appears granular
	39-5	KOH - 2x bromoform	87	43	2.0	shrunken and crumpled, surface obscured
	39-6	KOH - 2x bromoform	95	43	2.2	somewhat better preserved
	39-7	KOH - 2x bromoform	103	22	4.7	ditto

fibrous plant material, as in peat deposits, it is advisable to concentrate the pollen by dissolving some of the plant material. This can be quite easily accomplished by means of the acetolysis method described by Erdtman (1943). Where the deposit is largely inorganic, it is necessary to get rid of as much of the extraneous material as possible to effect a concentration of the pollen grains. The author has best been able to accomplish this by flotation in bromoform according to a procedure already described (Frey, 1951). The manner of treatment of the individual samples is listed in table 2. From the final concentrated sample one or more slides were prepared by mixing a small amount of the concentrate with glycerine jelly containing gentian violet.

The slides were examined for pollen and other microfossils at a magnification of 440 diameters. By means of a mechanical stage the slide was moved horizontally through the field of the microscope, and each pollen grain or spore was tabulated as encountered. The goal was to obtain 150 tree pollen grains from each level, according to standard procedure. In a number of instances, however, tree pollens were so scarce, even in the concentrated samples, that it would have required an excessive effort to comply with convention without commensurate increase in accuracy. This was particularly true in the two peat samples from Myrtle Beach State Park, and to a lesser extent in samples 39-5 and 39-6. The abundance factors listed in table 2 merely represent the average number of tree pollen grains found per horizontal traverse at high power and do not attempt to give the number of grains per unit volume or unit weight of sediment.

ANALYSIS OF HORRY CLAY

The overall results of the study are represented in table 3. As is customary in pollen analyses, each non-tree type of pollen or spore is expressed as a percentage of the total number of tree pollen grains found in the sample. The pollens and spores listed as "Unknowns" are either those that were clearly seen but not recognized by the author, or those that were so badly crumpled, fragmented, or obscured by granulations and internal clay particles that they were unrecognizable. For the most part these grains were not tricolpates, so that they would exert little or no effect on the percentage compo-

sition of the arboreal pollens. Only in samples 39-4 and 39-5 where the surface sculpturing was obscured and the pollen had a granular appearance, making tricolpate grains unidentifiable, is there any likelihood of an appreciable loss of tree pollens. These losses, however, are of a type that do not change the general interpretation of the results.

The tree pollen spectra in the Horry clay exhibit a progressive and orderly change from the lowest level to the uppermost. *Pinus* (pine), the most abundant tree pollen, comprises more than 90 per cent of the total tree pollens at either end of the section and only about 30 per cent in the middle. *Quercus* (oak), the next most abundant type, varies in a generally reciprocal manner, being least abundant at the top and bottom of the deposit and most abundant in the middle. Unfortunately for interpreting these changes, the species of oak and pine cannot be identified from their pollen grains, although attempts have been made by others (Cain, 1940) to identify pines on the basis of the size-frequency characteristics of fresh pollen of the various species. Such a wide variety of species of both pines and oaks with greatly differing ecological requirements occur in the Coastal Plain of the South Atlantic States that it is indeed lamentable more precise determinations cannot be made. However, other species and other pollen grains give clues as to the accompanying climatic conditions.

Excluding pine and oak which are present in all the samples, there is a greater diversity of the tree flora midway through the section than at either end. The types present in the middle of the deposit are such mesophytic types as *Nyssa* (tupelo), *Liquidambar* (sweetgum), *Fraxinus* (ash), *Ulmus* (elm), *Taxodium* (cypress), and *Salix* (willow). Climatic conditions were evidently moister, and probably also warmer, in the middle of the period than at both the beginning and end.

An increasing percentage of pine, like that in the upper half of the deposit, is probably an indication of cooling climate in the North Carolina-South Carolina region (Frey, 1951). If this cooling was antecedent to a glacial age, the climatic depression might have been sufficient to provide for the southward extension of *Picea* (spruce) and *Abies* (fir). Both of these types of pollens have been reported from Pleisto-

TABLE 3.

Pollen analysis of Horry clay and Myrtle Beach peat. All figures are expressed as percentages of total tree pollens.

	Myrtle Beach peat		Horry clay							
Pollen type	Upper peat	Lower peat	Stump sample	39-1	39-2	39-3	39-4	39-5	39-6	39-7
Pinus	36.7	58.2	95.6	81.5	79.3	30.7	53.5	52.9	79.0	93.2
Picea	42.0	3.6	0.3?							
Quercus	15.3	18.2	1.3	12.3	11.0	49.4	39.4	21.8	10.5	3.9
Carya	3.1	12.7	2.0	2.5		6.6	1.9	13.8	7.4	1.9
Liquidambar			0.7	1.2	1.9	6.0	2.6	3.4	1.1	
Nyssa	1.5	3.6		1.2	0.6	1.2		2.3	2.1	
Taxodium		3.6		1.2	5.2					
Betula	1.5				0.6		1.3			
Fraxinus					1.3	3.6				
Ulmus								2.3		1.0
Castanea							0.6			
Ostrya						2.4	0.6	2.3		
Salix								1.1		
Total tree pollens	65.5	55	151	81	155	166	155	87	95	103
Gramineae	1290	90.9		2.5	44.5	13.9	7.7	34.5	55.8	5.8
Compositae	146	43.6	0.7	2.5	3.2	0.6	7.7	14.9	24.2	1.9
Chenopodiaceae	1020	16.4	0.7	0.7			1.3			1.0
Cyperaceae	5.4			0.7	1.9		1.9		4.2	
Caryophyllaceae	10.8	12.7	0.7						2.1	
Aquatics										
Nuphar	20.6	7.3				1.2	0.6			
Nymphaea	5.4									
Myriophyllum	16.2					1.8		1.1		
Shrubs										
Ilex		3.6								
Rhus ?	20.6									
Myrica				0.7	1.3				1.1	
Corylus								1.1		
Ericaceae	5.4							2.3		
Alnus									1.1	
Pteridophytes										
Polypods	10.8	38.2						2.3	1.1	
Lycopods		5.5	0.7		0.6	3.6		3.4	5.3	1.0
Asplenium									3.2	
Isoetes ?		26.4								1.0
Sphagnum							0.6			
Unknowns	1000	28.7	3.3	70.4	59.3	100	100	26.4	94.8	28.1
Freshwater sponge spicules	—	—	—	+	+	+	+	+++	++	++

cene deposits in North Carolina (Buell, 1945; Frey, 1951) and South Carolina (Cain, 1944). The *Picea* in the sample around the cypress stumps is a doubtful record, because only a single half-grain of somewhat uncertain identity was found on the entire slide.

Taxodium pollen was found only in the two uppermost samples collected by Taber and not at all in the sample collected by the author from around the base of the cypress stumps. The pollen of cypress and swamp whitecedar is thin walled and apparently not so readily preserved as that of some of the other trees (Lewis and Cooke, 1927). It is consequently of interest that any recognizable cypress pollen was found, because of the great age of these sediments.

Carya (hickory) is present in all the samples except 39-2. There is quite a pronounced maximum of this tree type in the lower part of the deposit prior to the oak maximum. This is the same sequence observed by Frey (1951) in the pollen succession at Singletary Lake, N. C., during the most recent "postglacial" period. In this instance the hickory maximum was one stage in increasing dryness, culminating in the oak maximum, along with substantial percentages of grasses and composites. The shift from hickory to oak in the Horry clay seems not to represent similar changes in moisture conditions because of the contemporaneous occurrence of mesophytic types.

Pollen of three genera of freshwater aquatics (*Nuphar*, *Nymphaea*, and *Myriophyllum*) were found in small numbers in the middle portion of the deposit somewhat below the organic maximum. Moreover, monaxon flesh spicules of freshwater sponges were present in all samples except the uppermost, with a definite maximum in the three lowest samples. These two groups of fossil remains indicate freshwater basin deposition in the lower half of the section. Conditions of salinity in the upper half are obscure on the basis of the present material, although the decrease in abundance of sponge spicules may reflect either an absence of open water or an increase in salinity.

The pollen of grasses and composites is quite abundant in samples 39-2, 39-5, and 39-6. In the two latter samples there is also a representation of shrubs and pteridophytes. The overall interpretation of such conditions is that the surround-

ing land areas were only sparsely wooded, being covered rather with various herbs, shrubs, and ferns growing under fairly moist conditions edaphically and climatically.

ANALYSIS OF MYRTLE BEACH PEAT

The exact relationship of the seaside peat at Myrtle Beach State Park to the Horry clay is not known, although it is presumably younger. Very likely there was a considerable interval of time between the deposition of these two formations.

The presence of *Picea* pollen in both samples indicates the peat was laid down during a glacial period. There is little likelihood that spruce persisted in bogs during interglacial periods in this region, because Frey (1951) has shown that the spruce present in North Carolina in Wisconsin time disappeared rapidly and completely soon after the climate began to amelioriate after the Mankato maximum. Cain (1944) had already reported spruce (and fir) pollen from South Carolina in a number of buried soils. They, like the Myrtle Beach peat, are of uncertain age. The marked increase in percentage of spruce pollen in the upper peat may indicate that deposition began early in a glacial age and that climatic conditions became increasingly severe. In light of the Singletary Lake pollen diagrams (Frey, 1951) it is surprising to see the broadleaf trees so well represented during a glacial age.

Of equal interest to the occurrence of spruce pollen is the abundance of grasses, chenopods, and composites, especially in the upper peat. Such large percentages of chenopod and grass pollen in a coastal location can only mean that the peat was formed under salt marsh conditions. However, it is also apparent that there must have been some freshwater conditions as well, either alternating with brackish conditions or occurring simultaneously in separate basins. The species of aquatic plants are quite well represented with respect to the trees, and the mesophytic *Taxodium* and *Nyssa* are also present.

Very few tricolpate grains are included in the large number of unknowns in the upper peat sample. The types present are mainly smooth, acolpate grains of 3 sizes: a) the smallest might be moss spores; b) the medium-sized grains are about the size of *Juniperus*, and quite a number are monocolpate;

and c) the largest often have thick walls. Most of the grains tabulated as grass pollen were large, thin walled, with a prominent pore.

DISCUSSION

Spruce pollen in sediments of the South Atlantic coastal region is taken to indicate glacial time. Conversely, an absence of spruce pollen is taken to indicate interglacial time, and not merely a local recession of the glacier during Wisconsin time. Evidence for this generalization is the detailed pollen analysis of the sediments in Singletary Lake, N. C. (Frey, 1951), known by the radiocarbon method to extend through at least two of the interglacial sub-ages of Wisconsin time. Yet the climatic amelioration associated with these minor retreats of the ice was not sufficient in degree nor of long enough duration to completely eliminate spruce from the region, as indicated by the occurrence of its pollen in the sediments.

The prevailing opinion (Flint, 1947) is that the marine Pamlico formation was laid down during the mild Sangamon interglacial age, when the sea was approximately 25 feet higher than at present. Cooke (1937) considered the Horry clay to have been deposited during the early part of this interglacial age. According to this time relationship, one would expect to find indications of a warming climate in the pollen record of the Horry clay.

The climate was mild at this time but mainly in the middle of the section. Toward the top there was a deterioration of climate, as indicated by a progressive decline in broadleaf trees, particularly mesophytic types, and a progressive increase in pines. This evidence is contrary to the finding of polythermal marine diatoms in the upper part of the section, but these latter necessarily stem from marine environments, not terrestrial, and they may have been introduced by currents from more favorable localities. No unequivocal spruce pollen was found in the Horry clay samples.

The finding of spruce pollen in the Myrtle Beach peat indicates deposition during a glacial age. Along the Middle and South Atlantic coast of the United States there are quite a number of known peat deposits being eroded by the sea, sometimes at a depth up to 10 feet below mean low water.

Possibly all of these may date from the same glacial age as the Myrtle Beach peat. The peat at the Boylston Street fishweir, however, is not homologous, because its age is only about 5700 years (Flint and Deevey, 1951).

The radiocarbon age of the cypress stumps in the Horry clay is greater than 20,000 years (sample No. 105). This is taken by Flint and Deevey (1951) to indicate that the Pamlico formation does in fact date from the Sangamon interglacial age, because the only time since then that the sea level could have been higher than at present was during the thermal maximum, perhaps 7,000 years ago. Their reasoning obviously is based on the assumption that the Horry clay and the Pamlico formation both date from Sangamon time.

The stratigraphic relationship of the Myrtle Beach peat to the Pamlico formation and to the Horry clay is critical for interpreting the age of the latter. If the Horry clay is stratigraphically inferior to the peat, and hence chronologically older, then it would very likely date from Yarmouth time. But if the Horry clay and Pamlico formation were laid down in different interglacial ages, one would expect an erosional unconformity between them. Mansfield (1928) though there might be such an unconformity at the Neuse River site, but Cooke (1937) did not mention any unconformable relationship at the Inland Waterway site. Taber (correspondence) looked for an unconformity at the latter site but was unable to discover any. Hence, the stratigraphic evidence does not favor the interpretation that the Horry clay and Pamlico formation derive from different interglacial ages.

A more reasonable explanation might be that the Myrtle Beach peat, and similar deposits of the Atlantic Coast, were laid down in Wisconsin time, along the eroding edge of the Pamlico. In this case the peats are younger than the Pamlico, and there would be no mental compulsion to seek an unconformity between the Horry clay and Pamlico.

Cooke's interpretation of the conditions under which the Horry clay was formed was based entirely on the upper three feet of the deposit, which on the basis of the diatoms is entirely marine, except for the presence of the cypress stumps. He was unaware of the earlier freshwater portion of the

formation. His assumption that the upper part of the clay possibly represents a salt marsh deposit is not compatible with the results of the present study, in that there is a general lack of grasses and chenopods indicative of such deposits.

Granted on the basis of evidence other than pollen that the upper part of the clay was laid down under salt water conditions (although not salt marsh conditions), there still must have been at least one rather prolonged freshwater period to permit the cypress trees to become established and grow in such abundance. As to the cause of the sudden death of these cypresses, Cooke believed it was a reinvasion of salt water, and that the deposits laid down eventually buried most of the stumps still in their upright position. What the actual sequence of events was might be discovered by a pollen and diatom analysis of samples collected at intervals of no more than several centimeters.

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COMMUNICATION

OCCURRENCE OF SANTONIAN CRINOID IN WESTERN GULF REGION

While visiting localities mentioned in "The Geology of Bell County, Texas" (Adkins and Arick, 1930), a crinoid plate was found in the bank of South Darr's Creek, southern Bell County, Texas. I found another plate on Turnersville Creek, 1¾ miles south-southwest of Bluff Springs or 10 miles south of the State Capitol in Austin, Travis County, Texas. Both came from Austin chalk beds containing the brachiopod *Terebratulina guadalupae* Roemer, 1 to 2 feet below the ostreid *Exogyra laeviuscula* Roemer, which are within 10 feet below the base of the Burditt marl. Both specimens are basals or infrabasals of the free-floating crinoid, *Marsupites testudinarius americanus* Springer[1]. I wish to thank Dr. H. B. Stenzel, Bureau of Economic Geology, Austin, Texas, not only for his having kindly identified the first plate, but also for his guiding criticism of this note.

The species *Marsupites testudinarius* (Schlotheim) is restricted to the upper part of the *M. testudinarius* zone in Great Britain (Evans and Stubblefield, 1929), a stratigraphic unit that lies in the Upper Santonian in both Europe and America (Stephenson, 1923; Muller and Schenck, 1943). Since the American subspecies, *M. testudinarius americanus*, has been found also in the Tombigbee sand of Mississippi (Springer, 1911; Clark and Twitchell, 1915), the upper 10 feet of the Austin chalk, comprising the *Exogyra laeviuscula* zone and the upper part of the *Gryphaea aucella* zone (Young and Marks, MS, 1951), are regarded as equivalent to the Tombigbee sand and the Mooreville chalk of the eastern Gulf region (Monroe, 1947), and as Upper Santonian in age. This confirms the previous correlations which were made without use of this excellent intercontinental guide fossil.

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[1] *Marsupites americanus* Springer differs from *M. testudinarius* (Schlotheim) only in size and is consequently here regarded as a subspecies of the European form.

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ESSAY REVIEWS

Powell of the Colorado; by WILLIAM CULP DARRAH. Pp. ix, 426. Princeton, 1951 (Princeton University Press, $6.00).—John Wesley Powell was a phenomenal person. In the United States of the late nineteenth century there were few who could equal him in the range and quality of his deeds. Soldier, adventurer, scientist, executive, and reformer, Powell lived both the active and the intellectual life.

His adult life began seriously during the Civil War. A minie ball at bloody Shiloh destroyed his right hand and forearm, and left him a thirty-year legacy of recurring pain. He did not permit this horrible experience to terminate his military career. He continued his earnest service with the Army of the Tennessee, rose to be a major, and in his last battle—Nashville—served as chief of artillery under General George H. Thomas. In 1869 he led a party of men on a dangerous and exhausting passage of the Green and Colorado rivers, thus eliminating the last great pocket of unexplored territory in the continental United States. Thereafter, he made several original contributions to the science of geology and established himself as an outstanding authority on the public domain, and the leading expert of the nation on its irrigable lands. In the 1880s he administered two scientific organizations of the government—the U. S. Geological Survey and the Bureau of Ethnology. He guided the first hesitating steps of the government toward a reclamation policy and did not shrink from an honest appraisal of the prospects for irrigation in the west, although it meant antagonizing public opinion in that part of the country. After he had retired from the government, he projected several volumes of a philosophical work in which he hoped to unify all human knowledge. The biographer who would recapitulate and explain this manifold experience has given himself a herculean task.

In the absence of any formal collection of Powell papers, the author has had to do his own locating of research materials and he has gone to school, census, and court records, to newspapers, diaries, and letters. He also interviewed or communicated with scores of people who, for one reason or another, possessed information about Major Powell. This tireless and successful search will greatly facilitate the work of other students.

One fruitful result of the care for source materials is an excellent narrative chapter on the Powell expedition down the Green and Colorado rivers in 1869. As told by Mr. Darrah, the story has both clarity and excitement, and reflects his intimate acquaintance with the diaries and newspaper reports of this famous exploration.

Unfortunately, this high level of scholarship was not maintained.

If the author painstakingly uncovered facts, at the same time he was careless or indifferent about them. There are enough errors to justify a lack of confidence in the factual reliability of the biography. And he neglected almost completely the preeminent source for Powell's public life in Washington—the records of the U. S. Geological Survey in the National Archives, showing acquaintance with less than half a dozen of the tens of thousands of letters in that rich and voluminous collection. Consulting this obvious source would have introduced Mr. Darrah to important but hidden aspects of Powell's tenure of office in the Geological Survey, and also have grounded him so thoroughly in the history of the Survey that he could not easily have made some of the mistakes he did.

Structurally, this biography lacks cohesion. Except for the praiseworthy chapter on the descent of the Colorado, there is a disconnectedness about the narrative which makes it difficult to follow—for example, the journey of the Powell party to Pike's Peak in 1867 and the events at El Paso during the Irrigation Survey of 1888 to 1890. I think this defect could have been largely avoided had the author worked over his materials more thoroughly before he attempted to make a composition of them. Another weakness of organization is the miscellaneous character of some of the chapters. Instead of being tightly organized around one or at most two or three closely related topics, they tend to be conglomerations of every aspect of Major Powell's life; chapters 13 and 20 are the worst in this respect. Such chapters either irritate or tire the reader, as the undisciplined narrative confuses him.

A major objective of the biographer is the personality of his subject, but I do not think that a clear picture of Major Powell emerges from this volume. Descriptions of the man are few and inadequate; traits of his are mentioned, but not explained or developed; personal incidents tend to become simple conversations which the author has recreated with the aid of his imagination. From all reports, Major Powell had a strong personality, but here it is lost in the story of his activities and surroundings.

This interest in Major Powell as a person must, however, be secondary to the appreciation of him as an important figure in recent American history. Ultimately, the Major has significance because he became associated in a vital way with some of the underlying forces which have shaped modern American society. The primary responsibility of the biographer becomes, then, one of discovering and defining this relationship. For Major Powell, it means relating him to such decisive and complex factors as the growth of modern science, the settlement of the west, and the increasing importance of the government in national affairs.

I do not believe that Mr. Darrah has solved this problem of the man and his times. Major Powell is called "the real founder" of the U. S. Geological Survey when actually this important development in governmental science was a collective effort. As the papers of O. C. Marsh show, both he and Clarence King had decisive roles to play. The opponents of the move to consolidate the four western surveys do not receive a fair hearing. F. V. Hayden's position is distorted by too heavy a reliance upon one letter, and Lieutenant Wheeler's arguments for control of the scientific work in the west by the Corps of Engineers are not even given.

The same weakness in explanation or interpretation manifests itself in the account of Powell's first program to reclaim arid western lands, agitated by him between 1878 and 1880. It was "in the interest of all the people," while his antagonists represented "landed interests and big money interests." His proposals failed because they were "lost in the slow-moving machinery of government" and "the people themselves were not yet concerned with such an issue." As a matter of fact, popular sentiment had been aroused, but in opposition to the Major's ideas. Settlers viewed them as a threat to the security of their land titles and an obstacle to the rapid development of the west.

In the realm of the emotional and intellectual, neither Powell's intransigent agrarianism nor his transformation from an intense Methodist to a radical positivist are seriously analyzed.

In view of all these considerations, I can only conclude that here is an unsatisfactory biography. The life of Major Powell remains an inviting prospect for students of American history.

THOMAS G. MANNING

Geography of the USSR: A Regional Survey; by THEODORE SHABAD. Pp. xxxii, 584; maps, diagrams, tables. New York, 1951 (Columbia University Press, $8.50).

Geography of Russia; by N. T. MIROV. Pp. xi, 362; maps, diagrams. New York, 1951 (John Wiley & Sons, Inc., $6.50).

In recent years, a number of books on the geography of Russia have appeared. In general, they have treated the subject from the point of view of some aspect of the geographic discipline. Taken together, these works present a body of data primarily concerned with the physical elements of the Russian environment, and to a lesser extent with the "what and where" of economic distributions.

The two books reviewed here contribute to this general emphasis. They are, in fact, adequate representations of the kind of geographical interests which motivate most Soviet geographers.

It is quite clear that knowledge of the environmental complex within which a particular society develops and functions is an important aid to understanding that society's place in the global pattern. However, descriptive sketches of environmental features, whether physical or cultural, rarely reveal the subtle and constantly changing interrelationships that concern man, or their relevance to present day problems. This is particularly true of problems which arise in the context of the culture of Soviet Russia. Ways in which human actions in the USSR are related to aspects of geography have been superficially treated thus far in the literature. In a limited way, Mr. Shabad has considered this approach in his book. Both works, however, are fairly inclusive, heavily descriptive, encyclopedic compendiums of factual data little concerned with geographical interrelationships.

Obvious hindrances to an integrated treatment of Russian geography exist. One of these is simply the broad scope of the subject, acknowledged by both authors in their introductory remarks. More important, however, is the tendency among non-geographers generally, as well as among many non-geographically trained workers in the discipline, to regard descriptive treatments of areas of the earth's surface as the sum and substance of geography. Nor can one ignore the unfortunate political implications inherent in the consideration of the human geography of the Soviet Union by American geographers. The result of these and related factors is expressed in the emphasis upon descriptive treatments of the natural and human geographical complex of Russia, which dwells upon the nature of physical and cultural phenomena, largely skirting the reasons for their existence and distribution. Geography's purpose may not be to explain everything but it can and should go beyond description to include interpretation and analogous comparisons. This could provide the kind of insight into Russia and geography that would help to make the subtle and critical unknowns in that part of the world better known.

Mr. Shabad states in his foreword that his book is principally concerned with the "localization of the (Russian) economy." Other considerations enter into the author's sphere of interest, but primarily as related to political and economic aspects of this main focus. The dynamic nature of the geographical factors related to this subject make the task a difficult one. Soviet planning, dedicated to a rapid transformation of Russia from an agricultural

into a balanced industrial state, has compressed many changes in the natural and human geographical complex into the last thirty years. The resultant state of flux has acted in the past, and does now, to render any definitive pattern of economic distributions in that country quickly obsolescent. This does not suggest that major shifts in the basic economic framework occur easily or frequently. Resource distributions are largely fixed, and as a major element in the economic life of the nation contribute to a rigidity of its basic pattern. However, the development of new resources does lead to shifts in the center of gravity of economic activities, and it is the definitive expression of such changes in Russian geography that concern the author in this book.

Data pertinent to this interest are available but not neatly packed in the literature. In order to obtain the necessary material, one must examine innumerable articles that appear in the Soviet press and in related geographical, economic, and political publications. The results must then be organized so as to produce the outline of economic distributions desired. Technically, Mr. Shabad has utilized his method of charting political-administrative changes in the USSR to so organize these results, and to keep pace with the shifts in the economic center of gravity. Thus, the orientation of this book is to the present pattern of economic distributions, in which the author relates his conclusions to basic distributional patterns outlined by Soviet geographers, principally Baransky.

This ambitious work divides itself naturally into two parts. The first is introductory and consists of a general survey of elements of the physical complex, the political framework, and the economic pattern, as they are significant to this study. This section, while not integrally related to the rest of the book, establishes the systematic approach which is followed throughout. Chapter 1 includes all areas within the de facto limits of the USSR in 1950 in its consideration of the natural environment, and concludes with a section on mineral resources and distributions. Cultural influences upon place names are taken up in chapter 2, after delving into items of population and administrative-territorial divisions. The author considers changes in regional nomenclature to be strong indicators of political and economic developments, because they are closely tied to a fluid administrative-territorial structure. This relationship makes it possible to trace the political and economic life of various localities through fluctuation in their status. Place names indicate the economic activity of many such localities.

A presentation of planned and completed goals in agriculture completes the general survey. In this chapter, as in other instances throughout the book, Russian hopes for the future as well as past

accomplishments are transmitted somewhat uncritically. Reference to the shelter belt project intended to alter the micro-climate in drought ridden parts of the country is one such example. The accomplishments of Soviet agriculture in progressive exploitation of the arid lands is another. Consideration of the validity of the shelter belt concept, its feasibility in terms of capital and labor costs, or the results of similar undertakings elsewhere in the world are absent. No reference to geographical factors which favor or oppose application of experimental methods based upon the Dokuchaev-Kostichev-Williams system of agriculture to the dry lands is made. Perhaps extensive, detailed evaluations of Soviet plans and performance would be out of place, but comparisons of geographic factors and critical evaluations are needed. No measure is provided by which to gauge the relative value and meaning of these and other projects in their actual effect upon the economy, or their potential.

Regional surveys, based upon a division of the USSR into study units which conform to the political boundaries of the sixteen constituent union republics, comprise the second part of the study. Elements of the physical and cultural environments are synthesized in detailed descriptions of each unit. This treatment was considered by the author to be the most practical way to cover the country. Some readers can be expected to question the wisdom of the method, for the result is a volume in which the continuity is broken and the content heavily encyclopedic.

Each area is described in the manner outlined above for the first part of the book. The emphasis throughout is upon data relevant to economic localization, its extent, and types of production. As far as this treatment is concerned, the author has succeeded in his purpose to present an overall picture of the economic pattern and related political factors. This has been accomplished at the expense of other closely related considerations but not necessarily to the detriment of the author's main objective. The lack of greater emphasis upon the inter-relationships of economic activities throughout the USSR does seem, to this writer at least, to be an unfortunate omission.

To make the examination of the larger union republics more manageable, politically defined sub-regions and arbitrarily chosen areas have been set apart for individual treatment. Typical of this is the examination of the RSFSR, the largest and most important political region in the USSR. Here, oblasts, krays, and autonomous districts serve as study units, together with the arbitrarily defined "European West," "Central Industrial Region," "European Northwest," etc.

This volume is an outgrowth of the author's desire to remedy the basic lack of factual data relevant to the geographical aspect presented. It can serve as a valuable reference for students of Russian affairs for it is a comprehensive work containing many significant facts and details. It offers one of the most recent and up-to-date presentations of economic distributions in the USSR, including new information not previously published. Its text is not erudite, but as a whole is readable. The material is well selected and synthesized and the 54 outline maps are good. Tables are grouped in the appendix which, together with a good bibliography and index, concludes the work.

The organization of Mr. Mirov's book is in three parts. It begins with two introductory sections (chapters 1-9) outlining first the "General Picture of the Country." The author presents a brief treatment of the overall natural complex in about 50 pages. By word pictures the reader is moved along national boundaries and acquainted with elements of the physical and cultural landscape. Pertinent facts about dates of annexations and conquests, political-administrative divisions, heights and depths of rivers, seas, and dry-land forms are included. These elements are treated in greater detail in the latter part of the first section, with geological, climatic, faunal-floristic, and hydrological considerations.

A time sequence is introduced in the second section which begins with a glimpse into the "Historical Geography" of the territory now occupied by the Soviet Union. This chapter, with the historical past and not the geographical past of Russia as its focus, brings man into the picture. For the ensuing 22 pages several elements of the cultural complex are presented in the same loosely systematic manner used in the consideration of elements of the natural complex in the preceding section. Ethnic groups and their distributions, population and settlement, a kind of socioanthropological view of the relationships between blood and ethnic types, languages, and religions constitute the author's treatment of man on the Russian land.

The jacket of the book refers to the remaining 277 pages as the "meat" of Mr. Mirov's work. This section, and the last of the three parts, contains a detailed description of 20 geographic divisions. The technique employed is similar to that used in several of the sources to which the author refers in his introductory remarks. It is effective. The divisions are regional, representing Mr. Mirov's modification of L. S. Berg's basic and long accepted classifications dividing Russia into natural, latitudinal zones of lowland and mountain types. A modification of this system has

been needed for some time. In the opinion of this writer, floristic differentiations in Russia's biogeography indicate a general line of division between eastern and western parts of that country to exist roughly along the north-south trend of the Yenisei River. East of this river the land is geomorphologically distinct from the extensions of the European lowland to the west, and is largely within the sphere of permanently frozen ground. Moreover, and particularly important, the eastern lands are relatively undeveloped in respect to the cultural elements of the geographical complex. Significant growth of these elements has taken place in the eastern extension of the western lands, west of the Yenisei line, in recent time. In this respect, therefore, a dividing line appropriately indicating major physical and cultural differences could be drawn in the vicinity of the Yenisei which would more realistically separate Russia into its "European" and "Asiatic" parts than the older, less valid line along the Urals. Mr. Mirov's modification of the Berg system, however, does not concern itself with this. It is essentially a simplification of basic regional divisions, though not decreasing their number. This can be of value to the American reader interested in a more manageable macro-regional survey of Russian physiography.

Each of the remaining 20 chapters considers a regional subdivision systematically, covering factors of location, topography (including geological and hydrological considerations), climate. soils and vegetation, animal life, and a brief reference to man. The author has made particular effort to provide the kind of incidental and background information about various geographical features that the reader should have in order to understand them better in their Russian context. Particular emphasis is laid upon Russia's peripheral regions closest to America, in deference to current tensions between the two countries. One of the more worthwhile contributions of the work is the integration and presentation of the work of Russian investigators, little known outside the Soviet Union. Among these are Baransky, Suslov, Dobrynin, Bobrinsky, Zenkevitch, and others.

The book is not a popularization of geography in that it is severely restricted to the physical nature of the land, devoid of reference to related geographical aspects. The content is that of a limited general textbook, somewhat heavily written. The absence of a listing for the 34 maps and 26 tables distributed throughout the book is unfortunate. Its appearance now, however, is rather timely in view of the wide interest in the USSR.

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REVIEWS

Contributions to Mathematical Statistics; by R. A. FISHER. Edited by WALTER A. SHEWHART. Pp. 656. New York, 1950 (John Wiley & Sons, Inc., $7.50).—R. A. Fisher who is—according to Professor Harold Hotelling—"one of the greatest originators in the history of statistical methods" has now published a compilation of 43 of his papers on statistical research under the title *Contributions to Mathematical Statistics.* This book, together with the three books already published, gives a comprehensive account of the author's statistical lifework up to the present date. Many students and research workers, who are working in mathematical statistics, and to whom these papers have been unavailable because they can be found only in the largest libraries, have until now had to content themselves with the answer of R. A. Fisher's secretary: "One day, perhaps, a comprehensive collection of these papers will be published and made accessible to all those interested to read them."

Fisher's standard work on mathematical statistics, *Statistical Methods for Research Workers,* first published in 1925 (now in its 11th edition, Oliver & Boyd, Ltd., Edinburgh) has had a far-reaching influence on the statistical methods applied to agricultural and biological research, as well as to a wide range of subject matter in other fields. Fisher's second statistical main work, *The Design of Experiments* (5th ed., Oliver & Boyd, Ltd.), contains—according to F. Yates—"a full account of the logical basis of the whole technique of modern experimental design" (Imperial Bureau of Soil Science, Tech. Comm. 35), that is to say, wherever the statistical aspect is important. A third book, *Statistical Tables for Biological, Medical and Agricultural Research* (3rd ed., Oliver & Boyd, Ltd.), by R. A. Fisher and F. Yates, contains the tables of the two main works, together with a number of other tables for various statistical purposes with illustrations for their use.

Contributions to Mathematical Statistics appeared in 1950. This volume contains a selection of the author's papers on statistical research during the period 1920-1943.

Since it is impossible in a brief note to give a full account of these numerous and diverse papers, an attempt will be made to characterize some of the most ingenious advances in the theory of statistics for which the author is responsible: the logic of inductive inference (paper 26); the exact distribution in samples of the regression coefficient (paper 6), of the correlation coefficient and also of the partial and the multiple correlation coefficients. Fisher devised statistical theories for the application in agricultural experiments; he introduced the concept of the analysis of variance for the comparisons of yields of several varieties and many other purposes, the replication of field experiments, randomization and

the division of blocks into plots, as well as restricted randomization in arranging plots in a Latin Square. According to Wishart, "the Fisherian technique was something in the nature of a revolution and altered the subsequent course of agricultural experiments throughout the world." Fisher generalized "Student's" t-statistic to the z-statistic and was able with the help of this distribution to give a unified treatment of practically all the important distributions involved in testing Null-Hypotheses (biography by P. C. Mahalanobis and papers 1, 3, 14 and 17). He was one of the first to introduce the correct number of degrees of freedom from contingency tables (paper 5). He introduced the idea of "sufficiency" and defined the criterion for a sufficient statistic, as satisfied, when no other statistic that can be calculated from the same sample provides any additional information as to the value of the parameter to be estimated (paper 10). When a sufficient statistic exists it can always be obtained by "The Method of Maximum Likelihood"; this is Fisher's great achievement, it affords a comparison between observed and expected frequencies and leads to the calculation of Karl Pearson's Chi Square, the measure of discrepancy between them, and the fitting by the "Method of Maximum Likelihood" (paper 9). "Maximum Likelihood" is the general method of determination of the most probable value of which the Gaussian "Method of Least Squares" is a special case.

The reproduction of these papers is in the main photographic, except for new comments and corrections. DORA LUCKA

Negative Ions, 2d ed.; by H. S. W. MASSEY. Cambridge Monographs on Physics. Pp. xiv, 136; 31 figs. London and New York, 1950 (Cambridge University Press, $2.50).—This is the second edition of a well known book first published in 1937. It provides the conceptual and mathematical framework for an understanding of negative ions and their formation in gases, correlated skillfully with the experimental material available. The book has grown from 105 to 136 pages, mainly by the addition to the last chapter of discussions dealing with the role played by negative ions of hydrogen in solar radiation. HENRY MARGENAU

Petroleum Geology; by KENNETH K. LANDES. Pp. xi, 660. New York, 1951 (John Wiley & Sons, Inc., $10.00).—This book appears to be designed primarily as a textbook for students in petroleum geology but will also find wide use as a reference book for all workers in the field. It is divided into three sections. The first of these deals with the techniques of the petroleum geologist, the second with the geological occurrence of the petroleum, and the final

section with the oil and gas fields of the world and future sources of petroleum, both natural and synthetic.

The first part of the book is concerned with exploration and exploitation of natural petroleum sources. In his chapter on exploration the author describes all the techniques used on the surface by the geologist and also subsurface methods such as core drilling and geophysics. There are concise accounts of the various types of logs that are used in subsurface correlation and of structure contour, isopachous, lithofacies and other types of maps which are constructed from these data. The chapter on exploitation describes the different drives in oil pools as well as development and conservation practices such as spacing and unitization.

The section dealing with geologic occurrence of petroleum is the most interesting and rewarding. It is introduced by a very short chapter on the properties of petroleum at the surface and at depth. This chapter is the only disappointing one in the book. A more complete account of this important subject would be desirable. It is followed, however, by an excellent chapter on the origin of oil and gas in which all aspects of the problem are given full treatment and many hypotheses both of genesis and subsequent changes in the hydrocarbons are considered. The account is characterized throughout by the author's impartial approach and his hesitancy to commit himself to any one theory. A short chapter on the nature of reservoir rocks introduces the main part of this section which describes the different types of traps. They are classified into structural traps, caused by folding, faulting, and fissures, and variable permeability traps, caused by sedimentation, groundwater, truncation, and sealing. The main text explains the principles that govern accumulation in each trap type but the examples are set aside so that they do not interrupt the continuity of the account. Each example is on a separate page and consists of a concise description accompanied by many maps and cross sections to illustrate the structure. The larger maps are included with their field descriptions on sheets that fold into the book. An excellent feature of these accounts is that they each contain an index map of the state or country in which the field occurs indicating its position geographically and in relation to the other fields of the region.

The final section, comprising over three hundred pages, is a survey of the oil and gas fields of the United States and the rest of the world. The treatment of the fields in the United States is extensive and includes mention of all producing states and comprehensive accounts of such major producers as California and Texas. Each state is illustrated by maps of the tectonic framework and by several maps of the oil and gas fields. After a general discussion of

the types of accumulation in the state and the reservoirs that are important, the more productive of the fields are briefly reviewed. The same plan of presentation is continued in the description of the fields outside the United States but these are not covered in such detail. The organization of this whole section would be improved if the fields were not considered by artificial political units but by natural tectonic units. Landes' approach results in the consideration of the fields of the Illinois basin in both Illinois and Indiana sections. It also splits the salt dome fields of the Gulf Coast into the segments in Mexico, Texas, Mississippi, Louisiana, and Alabama.

An excellent feature of the whole book is the up-to-date material and the many references which are included in the footnotes. These footnotes provide a key to the literature on all phases of petroleum geology up to the summer of 1950 and indicate the large number of sources consulted in the preparation of this volume.

Landes' well prepared and interestingly written book is sure to find a good reception among teachers and students of petroleum geology. COLIN W. STEARN

Einfuehrung in die Mineralogie (Kristallographie und Petrologie); by CARL W. CORRENS. Pp. viii, 414; 405 figs., 1 plate. Berlin (Springer-Verlag, DM 41.60 bound, 38.00 in paper).—This textbook is based upon the fruitful premise that the interplay of crystallography and petrology (a "borderline field") should lead to new and valuable concepts. The success of the book in relating these fields cannot be denied, in spite of the formal division into three parts. The chapter headings may be freely translated as follows—Part I, Crystallography: 1, Crystal mathematics; 2, Crystal chemistry; 3, Crystal physics; 4, Crystal growth and solution. Part II, Petrology: 5, Physical-chemical concepts; 6, Magmatic rocks; 7, Weathering; 8, Sedimentary rocks; 9, Metamorphic rocks; 10, Geochemical conclusions. Part III, Appendix: A, Crystallographic tables; B, Properties of common minerals; C, Petrological tables; D, Bibliography. The tables in Part III (pp. 286-390) present most of the purely systematic descriptive material. The study of crystallization processes in the first section leads naturally to rock differentiation and mineral formation in the second. A complete table of contents (4 pages) and a thorough index of subjects and authors (24 triple-column pages) make the book an outstanding source for references and information on modern thinking in the field covered.

Excellent diagrams and photographs furnish appropriate illustrative material. Successive alternate pages or groups of pages are printed on two different grades of paper for economy of material

where type of illustrations permit. The location of pages by number is therefore inconvenient in the untrimmed paper edition. Mineralogists and petrologists will find the book a useful, thought-provoking addition to their libraries.

HORACE WINCHELL

PROJECTS IN GEOCHEMISTRY

At the recent meeting of the International Union of Chemistry in New York and Washington, the Commission on Geochemical Localization of the Elements, organized by the Section of Inorganic Chemistry, held its first meetings. It was agreed that one of the needs of the field could be met by having the Commission act as a central source of information on active research projects in geochemistry. It is therefore requested that persons and organizations that now have under way, or that expect in the near future to undertake research projects or bibliographic projects in the field of geochemistry, inform the Commission of these projects and their scope. Those in the Western Hemisphere should write to Dr. Michael Fleischer, U. S. Geological Survey, Washington 25, D. C.; those elsewhere should write to Professor T. F. W. Barth, Geological Museum, Oslo 45, Norway.

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Soil and Freshwater Nematodes; by T. Goodey. New York and London, 1951 (John Wiley & Sons, Inc., and Methuen & Co., Ltd., $7.00).

Directory of Washington Mining Operations 1951; by R. H. Stebbins. Washington State Division of Mines and Geology Information Circular 19. Olympia, 1951.

Johannes Kepler; by Carola Baumgardt. New York, 1951 (Philosophical Library, $3.75).

A New Theory of Gravitation; by Jacob Mandelker. New York, 1951 (Philosophical Library, $2.75).

Rabelais; by J. C. Powys. New York, 1951 (Philosophical Library, $3.75).

Evolution Emerging, A Survey of Changing Patterns from Primeval Life to Man, 2 vols.; by W. K. Gregory. New York, 1951 (The Macmillan Company, $20.00).

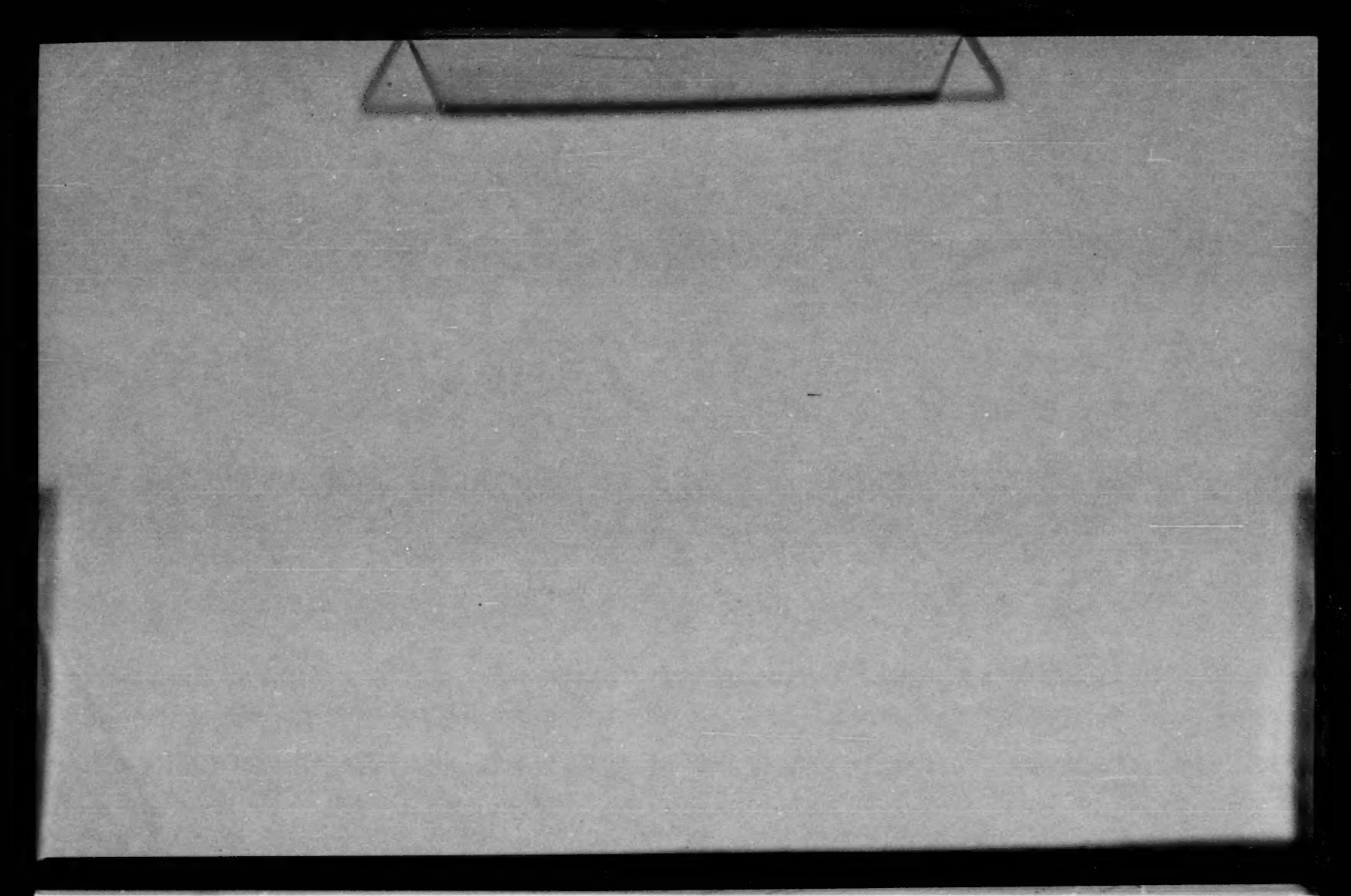
Experimental Spectroscopy, 2d ed.; by R. A. Sawyer. New York, 1951 (Prentice-Hall, Inc., $5.00).

Handbuch der Gletscherkunde und Glazialgeologie, Band 1, Allgemeiner Teil; Band 2, Historisch-regionaler Teil; by R. von Klebelsberg. Wien, 1948 and 1949 (Springer-Verlag, Band 1, $15.80, paper cover; $16.70, cloth bound; Band 2, $22.80, paper cover; $23.80, cloth bound; both volumes, $44.70, paper cover; $46.50, cloth bound).

The Beginnings of Diplomacy; by Ragnar Numelin. New York, 1951 (Philosophical Library, $12.00).

Optical Crystallography, 2d ed.; by E. E. Wahlstrom. New York, 1951 (John Wiley & Sons, Inc., $4.50).

Quantum Theory; by David Bohm. New York, 1951 (Prentice-Hall, Inc., $7.50).



Vol. 250 No. 3, 1952

CONTENTS

A Portion of the System Calcium Carbonate-Carbon Dioxide-Water, with Geological Implications
John P. Miller 161

Ice-ridged Moraines and their Relation to Glaciers
James L. Dyson 204

Pollen Analysis of the Horry Clay and a Seaside Peat Deposit near Myrtle Beach, S. C. . . . . *David G. Frey* 212

COMMUNICATION

Occurrence of Santonian Crinoid in Western Gulf Region
Edward Marks 226

ESSAY REVIEWS

Powell of the Colorado; by William Culp Darrah . . . . *Thomas G. Manning* 228

Geography of the USSR: A Regional Survey; by Theodore Shabad

Geography of Russia; by N T. Mikov . . . . . *Albert E. Burke* 230

REVIEWS

Contributions to Mathematical Statistics; by R. A. Fisher . . . . *Dora Lucka* 236

Negative Ions, 2d ed.; by H. S. W. Massey . . . . . *Henry Margenau* 237

Petroleum Geology; by Kenneth K. Landes . . . . . *Colin W. Stearn* 237

Einfuehrung in die Mineralogie (Kristallographie und Petrologie); by Carl W. Correns . . . . . *Horace Winchell* 239

Projects in Geochemistry 240

Publications Recently Received 240

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